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Adaptation of the Mechanism

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A SURROGATE SPECIES CHEMICAL REACTION MECHANISM FOR URBAN-SCALE AIR QUALITY SIMULATION MODELS

VOLUME I - ADAPTATION OF THE MECHANISM

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16. ABSTRACT

A surrogate species chemical mechanism has been refined, evaluated, and adapted for use in air quality simulation (AQS) models. The refined mechanism was evaluated against data from 491 environmental chamber experiments conducted in indoor and outdoor facilities. The results of the evaluation indicate that the mechanism's predictions are qualitatively and quantitatively consistent with data from a large number of single organic-NO_x and multi-organic-NO_x experiments. Subsequent to the testing of the mechanism, versions of the mechanism were adapted for use in single-cell models such as OZIPM/EKMA and multi-cell AQS models. Guidelines for using these mechanisms were also developed. The guidelines include specifying procedures for assignments of individual organic species to the chemical classes in the mechanisms and for selecting organic speciation profiles when ambient data are not available. Volume I describes the adaptation of the mechanism for AQS use; Volume II serves as the user's guide for implementing the mechanism in OZIPM/EKMA or multi-cell AQS.

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ABSTRACT

A surrogate species chemical reaction mechanism for the photooxidation of nonmethane organic compounds (NMOC) and nitrogen oxides (NO_x) has been developed for use in urban-scale photochemical air quality simulation (AQS) models. The chemical mechanism has been evaluated against data from 491 environmental chamber experiments conducted in indoor and outdoor facilities. The results of the mechanism evaluation indicate good model performance for a large number of single organic-NO_x and multi-organic NO_x experiments.

Two versions of the chemical mechanism have been adapted for use in photochemical AQS models. One version of the mechanism incorporates detailed representation of the reactions of NMOC and is suitable for use in single-cell AQS models such as the OZIPM/EKMA model. Another version of the mechanism incorporates a more condensed representation of the reactions of NMOC and is suitable for use in multi-cell Lagrangian and Eulerian AQS models. Under typical urban conditions, the two versions of the mechanism give very similar predictions for the concentrations of the key species involved in photochemical smog.

The approach used to model the complex mixture of NMOC with this mechanism is to use the chemical reactions of 12 common organic precursors as surrogates for the reactions of hundreds of different compounds. A system of assigning individual organic compounds to the most appropriate surrogate species has been developed. Also, speciated ambient NMOC data from surface stations in 25 urban areas and from aircraft samples collected upwind of four urban areas have been analyzed to develop default NMOC speciation profiles for use with this mechanism.

Sensitivity analysis using surrogate species mechanism in the OZIPM/EKMA model is reported. The relationships between model input parameters and the NMOC control requirement predictions are investigated. The input parameters included in the analysis are NMOC composition, NMOC/NO_x ratio, NMOC and ozone concentrations aloft, dilution rates, post-8 a.m. emission rates, future NO_x emission rates, present-day ozone concentrations, photolysis rates, and initial concentrations of peroxyacetylnitrate and nitrous acid.

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1. INTRODUCTION

Ozone concentrations downwind of most major metropolitan areas in the United States continue to exceed the one-hour national ambient air quality standard (0.12 ppm) under adverse meteorological conditions. In order to develop appropriate control strategies to reduce ambient ozone levels downwind of metropolitan areas, air quality control agencies need scientifically sound methods to relate maximum ozone concentrations to the emissions of ozone precursors, i.e., nonmethane organic compounds (NMOC) and nitrogen oxides (NO_x). The principal tools used in developing control strategies are photochemical air quality simulation (AQS) models. A critical component of the simulation model is the chemical reaction mechanism, which simulates the formation of ozone from NMOC and NO_x.

Numerous relatively up-to-date chemical mechanisms are currently used in urban-scale AQS models (Atkinson et al. 1982; Killus and Whitten 1982; Penner and Walton 1982; McRae et al. 1982; Whitten et al. 1985; Whitten and Gery 1986). While the mechanisms are largely based on the same body of laboratory kinetic and mechanistic data, different techniques and assumptions are used to represent the organic chemistry in the different mechanisms. Lumping of the organic compounds is necessary in all atmospheric photochemical mechanisms because it is computationally impossible to separately treat the large number of organic compounds found in ambient air. With the exception of the Carbon Bond mechanism (Whitten et al. 1983), which has been extensively tested in studies sponsored by the Environmental Protection Agency (EPA), these mechanisms have only been subjected to limited testing (15 to 35 experiments) against environmental chamber data. The precision and accuracy of these mechanisms are a major concern because they predict significantly different emission control requirements for identical meteorological, emissions, and background air quality conditions (Carter et al. 1981; Jeffries et al. 1981; Shafer and Seinfeld 1985).

Differences in the organic chemistry incorporated into the mechanisms are primarily responsible for the differences in emission control requirement predictions (Leone and Seinfeld 1984). Differences in the assumptions used to test the mechanisms against chamber data may also contribute to differences in control strategy predictions. Since progress toward reducing the uncertainties of atmospheric chemistry of organics is proceeding slowly, numerous researchers have recommended using two or more chemical mechanisms in control strategy modeling to allow uncertainties in the chemistry to be taken into account (Shafer and Seinfeld 1985; EPA 1987). Furthermore, the chemical mechanisms used in control strategy modeling should be tested extensively, rather than selectively, against the available environmental chamber data base. This data base of experiments has grown substantially in the last five years.

In recognition of the need for a well-tested and chemically up-to-date alternative to the Carbon Bond mechanism, the EPA contracted ERT, Inc., and the Statewide Air Pollution Research Center (SAPRC) at the University of California, Riverside, to carry out a research program to update and evaluate the Atkinson et al. (1982) mechanism (Phase I) and adapt the updated mechanism to AQS models (Phase II). The EPA chose the Atkinson et al. 1982 mechanism because they considered the surrogate species lumping approach employed in that mechanism to be the most viable alternative to the carbon bond lumping approach. This report describes the technical work performed in Phase II of the research program.

An updated surrogate species chemical mechanism was developed in Phase I of the program based on the Atkinson and Lloyd (1984) review and the mechanism of Lurmann et al. (1984, 1986) that, in turn, is an update of the Atkinson et al. (1982) mechanism. This mechanism was extensively tested against environmental chamber data from four facilities. The development of the mechanism and the details of the testing program are documented in a report on Phase I of this program entitled "Development and Testing of a Surrogate Species Chemical Reaction Mechanism, Volumes I and II" (Carter et al. 1986). Some minor changes in the detailed mechanism were implemented after the Phase I reports went to press, so the final mechanism and final results of the evaluation are presented in this report on Phase II of the research program.

The overall objective of Phase II was to adapt the mechanism for use in atmospheric AQS models. The specific tasks carried out in Phase II include:

1) Development of condensed versions of the mechanism for use in EPA's OZIPM model (used in conjunction with the Empirical Kinetic Modeling Approach (EKMA)) and for use in more sophisticated AQS models such as the Urban Airshed Model (UAM);

2) Development of guidelines for the speciation of NMOC into the organic classes employed in the mechanism, including analysis of ambient NMOC data collected in urban areas to determine speciation profiles for applications without site-specific data;

3) Sensitivity analysis of the OZIPM model (with the updated mechanism) to plausible input parameter variations for identification of the parameters that strongly influence the control requirement predictions; and

4) Development of standard test problems so that users can confirm that they have properly implemented the chemical mechanism in the chemical module of AQS models.

The results of tasks 1-3 are described in Volume I of this report. The results of task 4 are presented in Volume II along with a summary of the guidelines for using the mechanism in AQS models.

2. EVALUATION OF THE MECHANISM

Several modifications of the detailed chemical mechanism reported in Carter et al. (1986) were made in Phase II of the program. These modifications were significant enough to necessitate reevaluation of the detailed mechanism's performance against the environmental chamber data. The modifications of the detailed mechanism and the results of the evaluation are summarized in this section. Except where noted, the mechanism, data, and methods used in the evaluation were identical to those described in Carter et al. (1986). The Phase II evaluation included seventy additional chamber experiments that were not available during the Phase I testing program. This brings the total number of experiments to 490, which means this is by far the most comprehensive atmospheric chemical mechanism testing program performed in any research program.

2.1 The Detailed Chemical Mechanism

The detailed chemical mechanism used in Phase II of the program is shown in Tables 2-1 and 2-2. The species, reactions, rate constant expressions, and temperature dependent coefficients are listed. The quantum yield and absorption cross-section data for the photolytic reactions are identical to those reported in Carter et al. (1986), with the exception of those for NO_2. The NO_2 quantum yield data recommended by NASA (1985) and shown in Table 2-3 are used in the Phase II detailed mechanism. These data result in atmospheric NO_2 photolysis rates that are about 8% higher than those used in the Phase I mechanism. The updated atmospheric NO_2 photolysis rates and the ratios of the photolytic rates of other species to the NO_2 photolytic rate are shown in Table 2-4. These ratios have been computed using the solar actinic radiation intensities and spectral distributions reported by Peterson (1976) for zero elevation and best estimate albedo.

The Phase II detailed mechanism comprises 169 reactions and 65 species. Forty-eight of the species must be treated as integrated species in the kinetic solver. Three of the species (M, O_2, and H_2O) may be treated as constants and fourteen of the species can safely be treated

TABLE 2-1. SAPRC/ERT DETAILED CHEMICAL MECHANISM SPECIES LIST

SPECIES	ABREVIATION
1. NITRIC OXIDE	NO
2. NITROGEN DIOXIDE	NO2
3. OZONE	O3
4. NITROUS ACID	HONO
5. NITRIC ACID	HNO3
6. PERNITRIC ACID	HNO4
7. NITROGEN PENTOXIDE	N2O5
8. NITROGEN TRIOXIDE	NO3
9. HYDROPEROXY RADICAL	HO2
10. HYDROGEN PEROXIDE	H2O2
11. CARBON MONOXIDE	CO
12. FORMALDEHYDE	HCHO
13. ACETALDEHYDE	ALD2
14. PROPIONALDEHYDE	RCHO
15. PEROXYACETYLNITRATE	PAN
16. PEROXYPROPIONYL NITRATE	PPN
17. TOTAL RO2 RADICALS	RO2
18. TOTAL RCO3 RADICALS	RCO3
19. ORGANIC PEROXIDE	ROOH
20. ACETONE	ACET
21. METHYL ETHYL KETONE	MEK
22. GLYOXAL	GLYX
23. GLYOXAL PAN	GPAN
24. METHYL GLYOXAL	MGLY
25. GLYCOL ALDEHYDE	GCHO
26. GLYCOL ALDEHYDE PAN	PANG
27. PROPANE	ALK3
28. C4-C5 ALKANES	ALK4
29. C6+ ALKANES	ALK7
30. ALKYL NITRATES	ALKN
31. ETHENE	ETHE
32. PROPENE	PRPE
33. 1-BUTENE	OBUT
34. TRANS-2-BUTENE	TBUT
35. ISO-BUTENE	IBUT
36. BENZENE	BENZ
37. TOLUENE	TOLU
38. M-XYLENE	XYLE
39. 1,3,5 TRI-M-BENZENE	TMBZ
40. DICARBONYLS	DIAL
41. O-CRESOL	CRES
42. PHENOLS	PHEN
43. NITROPHENOLS	NPHE
44. DICARBONYLS	BGLY
45. BENZALDEHYDE	BCHO
46. BENZALDEHYDE PAN	PBZN
47. DI-NITROPHENOLS	DNPH

STEADY STATE SPECIES

48. OXYGEN - SINGLET D	O*SD
49. OXYGEN - ATOMIC	O
50. HYDROXYL RADICAL	OH
51. ACETALDEHYDE RCO3	MCO3
52. PROPIONALDEHYDE RCO3	PCO3
53. GLYOXAL RCO3	GCO3
54. GLYCOL ALDEHYDE RCO3	GAO3
55. GENERAL RO2 #1	RO2R
56. GENERAL RO2 #2	R2O2
57. MEK RO2	MKO2
58. ALKYL NITRATE RO2	RO2N
59. PHENOL RO2	RO2P
60. BENZALDEHYDE N-RO2	BZN2
61. BENZALDEHYDE RCO3	BAO3
62. PHENOXY RADICAL	BZO

CONSTANT SPECIES

63. MOLECULAR OXYGEN	O2
64. AIR	M
65. H2O VAPOR	H2O

TABLE 2-2. SAPRC/ERT DETAILED CHEMICAL MECHANISM

	REACTION	MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
1.	NO2 + HV ---> NO + O	RADIATION DEPENDENT		
2.	O + O2 + M ---> O3 + M	6.12E-34	2.23E-05	3.00E-28/(T**2.3)
3.	O + NO2 ---> NO + O2	9.30E-12	1.37E+04	
4.	O + NO2 + M ---> NO3 + M	9.12E-32	3.32E-03	8.10E-27/(T**2.0)
5.	NO + O3 ---> NO2 + O2	1.81E-14	2.68E+01	1.80E-12*EXP(-1370/T)
6.	NO2 + O3 ---> NO3 + O2	3.23E-17	4.77E-02	1.20E-13*EXP(-2450/T)
7.	NO + NO3 ---> 2.NO2	1.86E-11	2.75E+04	8.00E-12*EXP(252/T)
8.	NO + NO + O2 ---> 2.NO2	1.95E-38	7.09E-10	3.30E-39*EXP(529/T)
9.	NO2 + NO3 ---> N2O5	1.17E-12	1.73E+03	SEE NOTE 1
10.	N2O5 ---> NO2 + NO3	3.47E-02	2.08E+00	1.06E 27*EXP(-11354/T)*(300/T)*R9
11.	N2O5 + H2O ---> 2.HNO3	1.00E-21	1.48E-06	
12.	NO2 + NO3 ---> NO + NO2 + O2	4.04E-16	5.98E-01	2.50E-14*EXP(-1229/T)
13.	NO3 + HV ---> NO + O2	RADIATION DEPENDENT		
14.	NO3 + HV ---> NO2 + O	RADIATION DEPENDENT		
15.	O3 + HV ---> O + O2	RADIATION DEPENDENT		
16.	O3 + HV ---> O*SD + O2	RADIATION DEPENDENT		
17.	O*SD + H2O ---> 2.OH	2.20E-10	3.25E+05	
18.	O*SD + M ---> O + M	2.90E-11	4.29E+04	
19.	NO + OH ---> HONO	6.73E-12	9.94E+03	SEE NOTE 1
20.	HONO + HV ---> NO + OH	RADIATION DEPENDENT		
21.	NO2 + H2O ---> HONO - NO2 + HNO3	4.00E-24	5.91E-09	
22.	NO2 + OH ---> HNO3	1.16E-11	1.71E+04	SEE NOTE 1
23.	HNO3 + OH ---> NO3	1.28E-13	1.89E+02	9.40E-15*EXP(778/T)
24.	CO + OH ---> HO2	2.18E-13	3.22E+02	
25.	O3 + OH ---> HO2 + O2	6.78E-14	1.00E+02	1.60E-12*EXP(-942/T)
26.	NO + HO2 ---> NO2 + OH	8.28E-12	1.22E+04	3.70E-12*EXP(240/T)
27.	NO2 + HO2 ---> HNO4	1.39E-12	2.05E+03	SEE NOTE 1
28.	HNO4 ---> NO2 + HO2	8.41E-02	5.05E 00	4.29E 26*EXP(-10876/T)*R27
29.	HNO4 + OH ---> NO2 + H2O + O2	4.00E-12	5.91E+03	
30.	O3 + HO2 ---> OH + 2.O2	2.01E-15	2.96E+00	1.40E-14*EXP(-579/T)
31.	HO2 + HO2 ---> H2O2 + O2	1.76E-12	2.59E+03	2.20E-13*EXP(619/T)
32.	HO2 + HO2 + M ---> H2O2 + O2	5.13E-32	1.87E-03	1.90E-33*EXP(982/T)
33.	HO2 + HO2 + H2O ---> H2O2 + O2 + H2O	3.96E-30	1.44E-01	3.10E-34*EXP(2818/T)
34.	HO2 + HO2 + H2O ---> H2O2 + O2 + H2O	2.84E-30	1.04E-01	6.60E-35*EXP(3180/T)
35.	NO3 + HO2 ---> HNO3 + O2	1.76E-12	2.59E+03	2.20E-13*EXP(619/T)
36.	NO3 + HO2 + M ---> HNO3 + O2	5.13E-32	1.87E-03	1.90E-33*EXP(982/T)
37.	NO3 + HO2 + H2O ---> HNO3 + O2 + H2O	3.96E-30	1.44E-01	3.10E-34*EXP(2818/T)
38.	NO3 + HO2 + H2O ---> HNO3 + O2 + H2O	2.84E-30	1.04E-01	6.60E-35*EXP(3180/T)
39.	H2O2+ HV ---> 2.OH	RADIATION DEPENDENT		
40.	H2O2+ OH ---> HO2 + H2O	1.66E-12	2.45E+03	3.10E-12*EXP(-187/T)
41.	RO2 + NO ---> NO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
42.	RCO3 + NO ---> NO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
43.	RCO3 + NO2 ---> NO2	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
44.	RO2 + HO2 ---> HO2	3.00E-12	4.43E+03	
45.	RCO3 + HO2 ---> HO2	3.00E-12	4.43E+03	
46.	ROOH + HV ---> HO2 + OH	RADIATION DEPENDENT		

TABLE 2-2. SAPRC/ERT DETAILED CHEMICAL MECHANISM (CONTINUED)

	REACTION	MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
47.	RO2 + RO2 --->	1.00E-15	1.48E+00	
48.	RO2 + RCO3 --->	3.00E-12	4.43E+03	
49.	RCO3 + RCO3 --->	2.50E-12	3.69E+03	
50.	HCHO + HV ---> 2.HO2 + CO	RADIATION DEPENDENT		
51.	HCHO + HV ---> CO + H2	RADIATION DEPENDENT		
52.	HCHO + OH ---> HO2 + CO + H2O	9.00E-12	1.33E+04	
53.	HCHO + HO2 ---> RO2R + RO2	1.00E-14	1.48E+01	
54.	HCHO + NO3 ---> HNO3 + HO2 + CO	5.97E-16	8.82E-01	6.00E-13*EXP(-2060/T)
55.	ALD2 + OH ---> MCO3 + H2O + RCO3	1.60E-11	2.36E+04	6.90E-12*EXP(250/T)
56.	ALD2 + HV ---> CO + RO2R + HO2 + RO2 + HCHO	RADIATION DEPENDENT		
57.	ALD2 + NO3 ---> HNO3 + MCO3 + RCO3	2.50E-15	3.69E+00	3.00E-13*EXP(-1427/T)
58.	MCO3 + NO ---> NO2 + RO2R + RO2 + HCHO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
59.	MCO3 + NO2 ---> PAN	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
60.	MCO3 + HO2 ---> ROOH + HCHO	3.00E-12	4.43E+03	
61.	MCO3 + RO2 ---> .5HO2 + HCHO + RO2	3.00E-12	4.43E+03	
62.	MCO3 + RCO3 ---> HO2 + HCHO + RCO3	2.50E-12	3.69E+03	
63.	PAN ---> MCO3 + NO2 + RCO3	3.68E-04	2.21E-02	2.00E+16*EXP(-13542/T)
64.	RCHO + OH ---> RCO3 + PCO3	1.98E-11	2.93E+04	8.50E-12*EXP(252/T)
65.	RCHO + HV ---> RO2R + HO2 + CO + RO2 + ALD2	RADIATION DEPENDENT		
66.	RCHO + NO3 ---> HNO3 + PCO3 + RCO3	2.46E-15	3.63E+00	3.00E-13*EXP(-1432/T)
67.	PCO3 + NO ---> RO2R + NO2 + RO2 + ALD2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
68.	PCO3 + NO2 ---> PPN	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
69.	PCO3 + HO2 ---> ROOH + ALD2	3.00E-12	4.43E+03	
70.	PCO3 + RO2 ---> .5HO2 + ALD2 + RO2	3.00E-12	4.43E+03	
71.	PCO3 + RCO3 ---> HO2 + ALD2 + RCO3	2.50E-12	3.69E+03	
72.	PPN ---> PCO3 + NO2 + RCO3	3.68E-04	2.21E-02	2.00E+16*EXP(-13542/T)
73.	ACET + HV ---> MCO3 + RO2R + RCO3 + RO2 + HCHO	RADIATION DEPENDENT		
74.	ACET + OH ---> RO2R + RO2 + MGLY	2.29E-13	3.39E+02	1.00E-11*EXP(-1125/T)
75.	MEK + HV ---> MCO3 + RO2R + RCO3 + RO2 + ALD2	RADIATION DEPENDENT		
76.	MEK + OH ---> MKO2 + .5R2O2 + 1.5RO2 + .5HCHO + .5ALD2	9.85E-13	1.46E+03	1.20E-11*EXP(-745/T)
77.	MKO2 + NO ---> NO2 + .5MCO3 + .5PCO3 + RCO3	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
78.	MKO2 + HO2 ---> ROOH + .5HCHO + .5ALD2	3.00E-12	4.43E+03	
79.	MKO2 + RO2 ---> .5HO2 + .5HCHO + .5ALD2 + RO2	1.00E-15	1.48E+00	
80.	MKO2 + RCO3 ---> .5HO2 + .5HCHO + .5ALD2 + RCO3	3.00E-12	4.43E+03	
81.	GLYX + HV ---> .13HCHO +1.87CO	RADIATION DEPENDENT		
82.	GLYX + OH ---> .63HO2 +1.26CO + .37GCO3 + .37RCO3	1.15E-11	1.70E+04	
83.	GLYX + NO3 ---> HNO3 + .63HO2 +1.26CO + .37GCO3 + .37RCO3	6.01E-16	8.88E-01	6.00E-13*EXP(-2058/T)
84.	GCO3 + NO2 ---> GPAN	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
85.	GCO3 + NO ---> NO2 + HO2 + CO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
86.	GPAN ---> GCO3 + NO2 + RCO3	3.68E-04	2.21E-02	2.00E+16*EXP(-13542/T)
87.	GCO3 + HO2 ---> ROOH + CO	3.00E-12	4.43E+03	
88.	GCO3 + RO2 ---> .5HO2 + CO + RO2	3.00E-12	4.43E+03	
89.	GCO3 + RCO3 ---> HO2 + CO + RCO3	2.50E-12	3.69E+03	
90.	MGLY + HV ---> MCO3 + HO2 + CO + RCO3	RADIATION DEPENDENT		
91.	MGLY + OH ---> MCO3 + CO + RCO3	1.70E-11	2.51E+04	
92.	MGLY + NO3 ---> HNO3 + MCO3 + CO + RCO3	2.50E-15	3.69E+00	3.00E-13*EXP(-1427/T)

TABLE 2-2. SAPRC/ERT DETAILED CHEMICAL MECHANISM (CONTINUED)

	REACTION			MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
93.	GCHO + HV	--->	HCHO + 2.HO2 + CO	RADIATION DEPENDENT		
94.	GCHO + OH	--->	GAO3 + RCO3	2.30E-11	3.40E+04	
95.	GCHO + NO3	--->	HNO3 + GAO3 + RCO3	2.50E-15	3.69E+00	3.00E-13*EXP(-1427/T)
96.	GAO3 + NO2	--->	PANG	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
97.	GAO3 + NO	--->	NO2 + HO2 + HCHO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
98.	PANG	--->	GAO3 + NO2 + RCO3	3.68E-04	2.21E-02	2.00E+16*EXP(-13542/T)
99.	GAO3 + HO2	--->	ROOH + HCHO	3.00E-12	4.43E+03	
100.	GAO3 + RO2	--->	.5HO2 + HCHO + RO2	3.00E-12	4.43E+03	
101.	GAO3 + RCO3	--->	HO2 + HCHO + RCO3	2.50E-12	3.69E+03	
102.	ALK3 + OH	--->	RO2R + RO2 + .31RCHO + .69ACET	1.18E-12	1.75E+03	1.27E-17*EXP(14/T)*T**2.
103.	ALK4 + OH	--->	B01*HCHO +B02*ALD2 +B03*RCHO +B04*ACET +B05*MEK +B06*RO2N +B07*RO2R +B08*R2O2 +B09*RO2	3.22E-12 SEE NOTE 2	4.76E+03	1.05E-11*EXP(-353/T)
104.	ALK7 + OH	--->	B10*HCHO +B11*ALD2 +B12*RCHO +B13*ACET +B14*MEK +B15*RO2N +B16*RO2R +B17*R2O2 +B18*RO2	6.16E-12 SEE NOTE 2	9.11E+03	1.62E-11*EXP(-288/T)
105.	ALKN + OH	--->	NO2 +.155MEK +1.05RCHO + .48ALD2 + .16HCHO +1.39R2O2 +1.39RO2	2.03E-12	3.00E+03	2.19E-11*EXP(-709/T)
106.	RO2N + NO	--->	ALKN	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
107.	RO2N + HO2	--->	ROOH + MEK	3.00E-12	4.43E+03	
108.	RO2N + RO2	--->	RO2 + .5HO2 + MEK	1.00E-15	1.48E+00	
109.	RO2N + RCO3	--->	RCO3 + .5HO2 + MEK	3.00E-12	4.43E+03	
110.	R2O2 + NO	--->	NO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
111.	R2O2 + HO2	--->	ROOH	3.00E-12	4.43E+03	
112.	R2O2 + RO2	--->	RO2	1.00E-15	1.48E+00	
113.	R2O2 + RCO3	--->	RCO3	3.00E-12	4.43E+03	
114.	RO2R + NO	--->	NO2 + HO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
115.	RO2R + HO2	--->	ROOH	3.00E-12	4.43E+03	
116.	RO2R + RO2	--->	RO2 + .5HO2	1.00E-15	1.48E+00	
117.	RO2R + RCO3	--->	RCO3 + .5HO2	3.00E-12	4.43E+03	
118.	ETHE + OH	--->	RO2R + RO2 +1.56HCHO + .22GCHO	8.54E-12	1.26E+04	2.15E-12*EXP(411/T)
119.	ETHE + O3	--->	HCHO + .12HO2 + .42CO	1.74E-18	2.57E-03	1.20E-14*EXP(-2634/T)
120.	ETHE + O	--->	RO2R + HO2 + CO + RO2 + HCHO	7.29E-13	1.08E+03	1.04E-11*EXP(-792/T)
121.	ETHE + NO3	--->	R2O2 + RO2 + NO2 + 2.HCHO	1.10E-16	1.62E-01	2.00E-12*EXP(-2923/T)
122.	PRPE + OH	--->	HCHO + RO2 + RO2R + ALD2	2.63E-11	3.89E+04	4.85E-12*EXP(504/T)
123.	PRPE + O3	--->	.65HCHO + .5ALD2 +.165HO2 +.285CO + .06OH +.135RO2R +.135RO2	1.13E-17	1.67E-02	1.32E-14*EXP(-2105/T)
124.	PRPE + O	--->	.6ACET + .6RO2R + .2ALD2 + .2HO2 + .6RO2 + .4CO + .4HCHO	3.98E-12	5.88E+03	1.18E-11*EXP(-324/T)
125.	PRPE + NO3	--->	R2O2 + RO2 + HCHO + ALD2 + NO2	7.57E-15	1.12E+01	5.00E-12*EXP(-1935/T)
126.	OBUT + OH	--->	RO2R + RO2 + HCHO + RCHO	3.14E-11	4.64E+04	6.53E-12*EXP(468/T)
127.	OBUT + O3	--->	.5HCHO + .5RCHO +.165HO2 + .15ALD2 + .06OH +.135RO2R +.135RO2	1.10E-17	1.63E-02	3.46E-15*EXP(-1713/T)
128.	OBUT + O	--->	.44MEK + .39RCHO + .34HO2 + .17HCHO + .17CO + .17ALD2	4.19E-12	6.19E+03	1.25E-11*EXP(-326/T)
129.	OBUT + NO3	--->	RO2R + RO2 + HCHO + RCHO + NO2	9.67E-15	1.43E+01	5.00E-12*EXP(-1862/T)
130.	TBUT + OH	--->	RO2R + RO2 + 2.ALD2	6.37E-11	9.42E+04	1.01E-11*EXP(549/T)
131.	TBUT + O3	--->	ALD2 + .27RO2R + .12OH + .21HO2 + .3HCHO + .15CO + .27RO2	2.00E-16	2.96E-01	9.08E-15*EXP(-1137/T)

TABLE 2-2. SAPRC/ERT DETAILED CHEMICAL MECHANISM (CONTINUED)

		REACTION	MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
132.	TBUT + O	---> MEK + .4HO2	2.34E-11	3.45E+04	2.26E-11*EXP(10/T)
133.	TBUT + NO3	---> R2O2 + RO2 + NO2 + 2.ALD2	3.79E-13	5.61E+02	1.00E-11*EXP(-975/T)
134.	IBUT + OH	---> RO2R + RO2 + HCHO + ACET	5.14E-11	7.60E+04	9.51E-12*EXP(503/T)
135.	IBUT + O3	---> .5ACET + .5HCHO + .4MEK + .06HO2 + .10OH + .10RO2R + .10RO2 + .10MGLY	1.21E-17	1.78E-02	3.55E-15*EXP(-1694/T)
136.	IBUT + O	---> .5MEK + .5RCHO + .4HO2	1.52E-11	2.25E+04	1.76E-11*EXP(-43/T)
137.	IBUT + NO3	---> R2O2 + RO2 + ACET + HCHO + NO2	2.69E-13	3.98E+02	1.00E-11*EXP(-1077/T)
138.	BENZ + OH	---> .27PHEN + .27HO2 + .73RO2R + .73RO2 +.212GLYX + .65BGLY	1.28E-12	1.90E+03	7.57E-12*EXP(-529/T)
139.	BGLY + OH	---> GCO3 + RCO3	3.00E-11	4.43E+04	
140.	BGLY + HV	---> GCO3 + RCO3 + HO2	RADIATION DEPENDENT		
141.	TOLU + OH	---> .16CRES + .16HO2 + .08BCHO +.114GLYX +.144MGLY + .40DIAL + .84RO2R + .84RO2	6.19E-12	9.14E+03	2.10E-12*EXP(322/T)
142.	DIAL + OH	---> PCO3 + RCO3	3.00E-11	4.43E+04	
143.	DIAL + HV	---> HO2 + CO + MCO3 + RCO3	RADIATION DEPENDENT		
144.	XYLE + OH	---> .17CRES + .17HO2 + .04BCHO +.095GLYX + .83RO2 + .83RO2R +.316MGLY + .65DIAL	2.45E-11	3.62E+04	1.66E-11*EXP(116/T)
145.	TMBZ + OH	---> .17CRES + .17HO2 + .02BCHO + .86MGLY + .83RO2 + .83RO2R + .49DIAL	6.20E-11	9.16E+04	
146.	CRES + OH	---> .2MGLY + .15RO2P + .85RO2R + RO2	4.00E-11	5.91E+04	
147.	CRES + NO3	---> HNO3 + BZO	2.20E-11	3.25E+04	
148.	RO2P + NO	---> NPHE	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
149.	RO2P + HO2	---> ROOH	3.00E-12	4.43E+03	
150.	RO2P + RO2	---> RO2 + .5HO2	1.00E-15	1.48E+00	
151.	RO2P + RCO3	---> RCO3 + .5HO2	3.00E-12	4.43E+03	
152.	PHEN + OH	---> .2GLYX + .15RO2P + .85RO2R	2.80E-11	4.14E+04	
153.	PHEN + NO3	---> HNO3 + BZO	3.80E-12	5.62E+03	
154.	BZO + NO2	---> NPHE	1.50E-11	2.22E+04	
155.	BZO + HO2	---> PHEN	3.00E-12	4.43E+03	
156.	BZO	---> PHEN	1.00E-03	6.00E-02	
157.	NPHE + NO3	---> HNO3 + BZN2	3.80E-12	5.62E+03	
158.	BZN2 + NO2	---> DNPH	1.50E-11	2.22E+04	
159.	BZN2 + HO2	---> NPHE	3.00E-12	4.43E+03	
160.	BZN2	---> NPHE	1.00E-03	6.00E-02	
161.	BCHO + OH	---> BAO3 + RCO3	1.20E-11	1.77E+04	
162.	BCHO + HV	--->	RADIATION DEPENDENT		
163.	BCHO + NO3	---> BAO3 + HNO3 + RCO3	1.95E-15	2.89E+00	3.00E-13*EXP(-1500/T)
164.	BAO3 + NO	---> BZO + NO2 + RO2R + RO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
165.	BAO3 + NO2	---> PBZN	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
166.	PBZN	---> BAO3 + NO2 + RCO3	1.62E-04	9.74E-03	1.60E+15*EXP(-13033/T)
167.	BAO3 + HO2	---> ROOH + PHEN	3.00E-12	4.43E+03	
168.	BAO3 + RO2	---> .5HO2 + PHEN + RO2	3.00E-12	4.43E+03	
169.	BAO3 + RCO3	---> HO2 + PHEN + RCO3	2.50E-12	3.69E+03	

TABLE 2-2. SAPRC/ERT DETALIED CHEMICAL MECHANISM (CONTINUED)

NOTES:

1. Pressure and temperature dependent rate constants are determined from the expression

$$K = \frac{B(T^{**}C)M}{1 + \dfrac{B(T^{**}C)M}{D(T^{**}E)}} A^{**}EE, \quad EE = \frac{1.}{1 + \left(\mathrm{LOG10}\left(\dfrac{B(T^{**}C)M}{D(T^{**}E)}\right) \right)^{**}2}$$

Where:

Reaction	A	B	C	D	E
9	0.6	9.0E-20	-4.3	2.4E-11	-0.5
19	0.6	1.0E-22	-3.3	9.0E-09	-1.0
22	0.6	2.2E-22	-3.2	4.0E-08	-1.3
27	.56	5.71E-20	-4.6	1.34E-12	0.2

2. Alkane product coefficents are temperature dependent. They are determined by interpolation from the values at the following three temperatures.

Coeff.	270 K	300 K	330 K
B01	0.197	0.189	0.188
B02	0.168	0.315	0.582
B03	0.115	0.166	0.244
B04	0.351	0.339	0.350
B05	0.489	0.442	0.267
B06	0.114	0.073	0.050
B07	0.886	0.927	0.950
B08	0.446	0.599	0.807
B09	1.332	1.526	1.757
B10	0.005	0.023	0.054
B11	0.021	0.032	0.081
B12	0.215	0.249	0.296
B13	0.297	0.355	0.419
B14	0.765	0.882	0.891
B15	0.288	0.190	0.126
B16	0.701	0.810	0.873
B17	0.651	0.837	1.004
B18	1.352	1.647	1.877

TABLE 2-3

ABSORPTION CROSS-SECTION AND QUANTUM YIELD DATA FOR NO_2

Wavelength (um)	Absorption Cross-Section	Quantum Yield
0.295	9.670E-20	0.984
0.300	1.170E-19	0.980
0.305	1.660E-19	0.976
0.310	1.760E-19	0.972
0.315	2.250E-19	0.968
0.320	2.540E-19	0.964
0.325	2.790E-19	0.960
0.330	2.990E-19	0.956
0.335	3.450E-19	0.952
0.340	3.880E-19	0.948
0.345	4.070E-19	0.944
0.350	4.100E-19	0.940
0.355	5.130E-19	0.936
0.360	4.510E-19	0.932
0.365	5.780E-19	0.928
0.370	5.420E-19	0.85
0.375	5.350E-19	0.77
0.376	5.478E-19	0.78
0.377	5.606E-19	0.92
0.378	5.734E-19	0.82
0.379	5.862E-19	0.87
0.380	5.990E-19	0.90
0.381	5.980E-19	0.81
0.382	5.970E-19	0.70
0.383	5.960E-19	0.68
0.384	5.950E-19	0.70
0.385	5.940E-19	0.77
0.386	5.952E-19	0.84
0.387	5.964E-19	0.75
0.388	5.976E-19	0.81
0.389	5.988E-19	0.78
0.390	6.000E-19	0.80
0.391	5.978E-19	0.88
0.392	5.956E-19	0.84
0.393	5.934E-19	0.90
0.394	5.912E-19	0.90
0.395	5.890E-19	0.84
0.396	6.064E-19	0.83
0.397	6.238E-19	0.82
0.398	6.412E-19	0.77

TABLE 2-3 (continued)

Wavelength (um)	Absorption Cross-Section	Quantum Yield
0.399	6.586E-19	0.78
0.400	6.760E-19	0.68
0.401	6.672E-19	0.65
0.402	6.584E-19	0.62
0.403	6.496E-19	0.57
0.404	6.408E-19	0.42
0.405	6.320E-19	0.32
0.406	6.210E-19	0.33
0.407	6.100E-19	0.25
0.408	5.990E-19	0.20
0.409	5.880E-19	0.19
0.410	5.770E-19	0.15
0.411	5.876E-19	0.10
0.415	6.300E-19	0.067
0.420	6.230E-19	0.023
0.425	6.000E-19	0.000

TABLE 2-4. RATIO OF OTHER PHOTOLYTIC REACTION RATES TO THE NO2 PHOTOLYSIS RATE AT ZERO ELEVATION*

REACTION	SOLAR ZENITH ANGLE 0.	10.	20.	30.	40.	50.	60.	70.	78.	86.
NO3 + hv --> NO + O2	2.26E+00	2.26E+00	2.28E+00	2.32E+00	2.39E+00	2.56E+00	2.83E+00	3.34E+00	4.06E+00	2.79E+00
NO3 + hv --> NO2 + O	2.04E+01	2.05E+01	2.07E+01	2.11E+01	2.18E+01	2.31E+01	2.54E+01	2.97E+01	3.55E+01	2.58E+01
O3 + hv --> O + O2	5.52E-02	5.53E-02	5.56E-02	5.61E-02	5.71E-02	5.99E-02	6.45E-02	7.43E-02	8.90E-02	6.60E-02
O3 + hv --> O*SD + O2	4.56E-03	4.45E-03	4.12E-03	3.56E-03	2.86E-03	2.06E-03	1.26E-03	5.98E-04	2.80E-04	1.54E-04
HONO + hv --> NO + OH	1.96E-01	1.96E-01	1.96E-01	1.96E-01	1.94E-01	1.93E-01	1.90E-01	1.85E-01	1.81E-01	1.88E-01
H2O2 + hv --> 2.OH	9.08E-04	9.03E-04	8.82E-04	8.45E-04	7.91E-04	7.18E-04	6.25E-04	5.12E-04	4.31E-04	3.83E-04
ROOH + hv --> HO2 + OH	9.08E-04	9.03E-04	8.82E-04	8.45E-04	7.91E-04	7.18E-04	6.25E-04	5.12E-04	4.31E-04	3.83E-04
HCHO + hv --> 2.HO2 + CO	3.65E-03	3.62E-03	3.53E-03	3.36E-03	3.11E-03	2.77E-03	2.33E-03	1.81E-03	1.41E-03	1.10E-03
HCHO + hv --> CO + H2	5.59E-03	5.57E-03	5.50E-03	5.38E-03	5.19E-03	4.91E-03	4.51E-03	3.97E-03	3.57E-03	3.43E-03
ALD2 + hv --> CO + CH3O2	5.87E-04	5.79E-04	5.51E-04	5.01E-04	4.36E-04	3.53E-04	2.58E-04	1.63E-04	1.01E-04	5.98E-05
RCHO + hv --> CO + C2H5O2	1.19E-03	1.18E-03	1.14E-03	1.08E-03	9.94E-04	8.75E-04	7.26E-04	5.53E-04	4.27E-04	3.31E-04
ACET + hv --> MCO3 + HCHO	1.34E-04	1.32E-04	1.27E-04	1.18E-04	1.06E-04	8.97E-05	7.05E-05	4.98E-05	3.55E-05	2.49E-05
MEK + hv --> MCO3 + ALD2	1.91E-04	1.89E-04	1.82E-04	1.69E-04	1.51E-04	1.28E-04	1.01E-04	7.11E-05	5.07E-05	3.56E-05
GLYX + hv -->.13HCHO +1.87CO	7.79E-03	7.81E-03	7.87E-03	7.97E-03	8.17E-03	8.46E-03	8.97E-03	9.88E-03	1.09E-02	9.73E-03
MGLY + hv --> MCO3 + HO2 + CO	1.72E-02	1.72E-02	1.74E-02	1.76E-02	1.80E-02	1.87E-02	1.98E-02	2.17E-02	2.37E-02	2.14E-02
GCHO + hv --> HO2 + CH3O2+ CO	5.87E-04	5.79E-04	5.51E-04	5.01E-04	4.36E-04	3.53E-04	2.58E-04	1.63E-04	1.01E-04	5.98E-05
BGLY + hv --> GCO3 + HO2	4.78E-03	4.77E-03	4.72E-03	4.62E-03	4.47E-03	4.22E-03	3.94E-03	3.52E-03	3.22E-03	3.20E-03
DIAL + hv --> MCO3 + HO2 + CO	6.38E-02	6.36E-02	6.29E-02	6.15E-02	5.95E-02	5.66E-02	5.25E-02	4.70E-02	4.29E-02	4.27E-02
BCHO + hv -->	5.19E-03	5.18E-03	5.14E-03	5.09E-03	4.99E-03	4.85E-03	4.64E-03	4.36E-03	4.14E-03	4.23E-03

* The NO2 photolysis rate (per second) at zero elevation is

NO2 + hv --> NO + O	8.29E-03	8.22E-03	8.02E-03	7.66E-03	7.10E-03	6.26E-03	5.05E-03	3.32E-03	1.64E-03	3.51E-04

as steady-state species if the kinetic solver package in which the mechanism is used can accommodate these types of species. The organic precursor species included in the mechanism are propane, C4-C5 alkanes, >C5 alkanes, ethene, propene, 1-butene, trans-2-butene, isobutene, benzene, toluene, m-xylene, and mesitylene. The rate constants and product coefficients for the lumped alkane mechanisms are based on the explicit mechanisms for compounds in these classes. The C4-C5 alkane reactions are based on equal weighting of the kinetic and product data for the reactions of n-butane, n-pentane, iso-butane, and iso-pentane. The >C5 alkane reactions are based on equal weighting of the kinetic and product data for the reactions of n-hexane, n-heptane, n-octane, 2,3-dimethylbutane, 2-methylpentane, 2,3-dimethylpentane, and iso-octane. The selection of these surrogates was based on the analysis of automobile exhaust speciation performed in Phase I. The oxygenated products in the mechanism include formaldehyde, acetaldehyde, glycol aldehyde, propionaldehyde, benzaldehyde, acetone, methylethylketone, glyoxal, methyl glyoxal, and two surrogate species for the unknown ring-opening products of aromatic oxidation.

In assembling the Phase II detailed mechanism, a condensation technique was employed to reduce the number of individual peroxy radicals included in the Phase I detailed mechanism. The technique is primarily intended to represent the peroxy radical reactions in the presence of NO_x. In order to minimize the number of species that must be integrated in the mechanism, most individual peroxy radicals formed in the photooxidations of the various organics are not explicitly included in the mechanism. Instead, in any reaction forming them, the peroxy radicals are replaced by the set of stable products expected to be ultimately formed when they react in the presence of NO, and one or more generalized peroxy radical pseudo species. The pseudo species are used to represent the effects of the reactions of the individual peroxy radicals. The effects are common to large groups of peroxy radicals, such as the conversion of NO to NO_2 when they react with NO, etc. This is applied not only to individual peroxy radicals, but also to groups of peroxy radicals formed from the same species, whose overall reactions are lumped together in the mechanism. The specific peroxy pseudo species used in this mechanism and the overall common processes they represent are shown in Table 2-5 (see also reactions 77-80, 106-117, and 148-151 in Table 2-2).

As an example of this technique, consider the photooxidation of n-butane. In the presence of NO at 300°K, the n-butane photooxidation process is as follows:

$$\mathrm{OH + n\text{-}butane \xrightarrow{O_2} 0.15\ CH_3CH_2CH_2CH_2OO. + .85\ CH_3CH(OO.)CH_2CH_3}$$

$$\mathrm{CH_3CH_2CH_2CH_2OO. + NO \longrightarrow 0.03\ RONO_2 + 0.97\ (NO_2 + CH_3CH_2CH_2CH_2O.)}$$

$$\mathrm{CH_3CH(OO.)CH_2CH_3 + NO \longrightarrow 0.08\ RONO_2 + 0.92\ (NO_2 + CH_3CH(O.)CH_2CH_3)}$$

$$\mathrm{CH_3CH_2CH_2CH_2O. \xrightarrow{O_2} 0.78\ HOCH_2CH_2CH_2CH_2OO. + 0.22\ (RCHO + HO_2.)}$$

$$\mathrm{CH_3CH(O.)CH_2CH_3 \xrightarrow{O_2} 0.63\ (MEK + HO_2) + 0.37\ (CH_3CHO + C_2H5OO.)}$$

$$\mathrm{HOCH_2CH_2CH_2CH_2OO. + NO \xrightarrow{O_2} NO_2 + HO_2. + (bifunctional\ product,\ represented\ by\ RCHO + 0.25\ MEK)}$$

$$\mathrm{C_2H_5OO. + NO \xrightarrow{O_2} NO_2 + HO_2. + CH_3CHO}$$

If the peroxy and alkoxy radical intermediates are approximately in steady-state (which test calculations have shown to be a good approximation in the presence of NO_x and sunlight), then the following reaction has the same net effect as the reactions above:

$$\begin{aligned}\mathrm{OH + n\text{-}butane} \longrightarrow\ & \mathrm{0.07\ (RONO_2 - NO) + 0.93\ (NO_2 + HO_2 - NO)\ +} \\ & \mathrm{0.40\ (NO_2 - NO) + 0.57\ CH_3CHO + 0.52\ MEK\ +} \\ & \mathrm{0.15\ RCHO}\end{aligned}$$

TABLE 2-5

PEROXY RADICAL PSEUDO-SPECIES USED IN THE MECHANISM TO REPRESENT OVERALL PROCESSES COMMON TO PEROXY RADICAL REACTIONS

Pseudo-Species Name	Products Formed		
	Reaction with NO	Reaction with HO2	Reaction with RO2/RCO3
RO2R	NO2 + HO2	-OOH	0.5 HO2
R2O2	NO2	none	none
RO2N	RONO2	-OOH + MEK	0.5 HO2 + MEK
RO2P	Nitrophenol	-OOH + (inert)	0.5 HO2 + (inert)
MKO2	NO2 + CH3CO3.	-OOH + HCHO + CO2	0.5 HO2 + HCHO + CO2

From Table 2-5, it can be seen that these processes can be represented without any negative product species by the following reaction:

$$\text{OH} + \text{n-butane} \longrightarrow 0.07\ \text{RO2N} + 0.93\ \text{RO2R} + 0.40\ \text{R2O2} + 0.57\ \text{CH}_3\text{CHO} + 0.52\ \text{MEK} + 0.15\ \text{RCHO}$$

This reaction shows how the photooxidation of n-butane at 300°K is represented in the Phase II detailed mechanism. This technique was applied in an entirely analogous manner to the reactions of other radicals or groups of radicals to minimize the number of individual peroxy radicals in the mechanism.

Significant changes were made to the aromatic oxidation mechanism employed in Phase II. In order to appreciate the rationale for these changes, background information on the aromatic oxidation mechanism is provided in addition to a description of the changes.

As previously noted, the aromatic hydrocarbons are represented by benzene, toluene, m-xylene, and mesitylene (or 1,3,5-trimethyl benzene) in the mechanism. The aromatic reactions are based on those formulated by Atkinson et al. (1980, 1982), Atkinson and Lloyd (1984), Leone and Seinfeld (1984), Leone et al. (1985), and Lurmann et al. (1986), but the reactions were modified to be consistent with the recently observed α-dicarbonyl yields, to include a parameterized representation of the uncharacterized aromatic ring opening products, and to delete the aromatic nitrate formation reaction, which was assumed to occur from the reactions of NO with the aromatic peroxy radical intermediates.

Despite continuing studies of aromatic photooxidation mechanisms, the current understanding of the ring opening reactions following the initial attack by OH radicals on the aromatic rings and the nature and reactions of most of the products formed continues to be grossly inadequate. Indeed, the most recent experimental data have tended to raise more questions in this regard than they have answered, giving results that are inconsistent with previously published aromatic photooxidation mechanisms. In particular, the recent experimental data concerning the yields of α-dicarbonyls from benzene and the methyl-substituted benzenes obtained by Tuazon et al. (1986) and Bandow and co-workers (Bandow et al. 1985; Bandow and Washida 1985a,b) indicate yields of α-dicarbonyls that are significantly lower than predicted by any of the previous mechanisms (Atkinson et al. 1982; Killus and Whitten 1982; Atkinson and Lloyd 1984; Leone and Seinfeld 1984; Leone et al. 1985; Whitten et al. 1985; Lurmann et al. 1986). These experimental data, coupled with the observations of several unsaturated oxygenates as products from toluene (Dumdei and O'Brien 1984; Shepson et al. 1984) and o-xylene (Shepson et al. 1984), are not consistent with the ring-opening mechanisms proposed previously (Atkinson and Lloyd 1984; Leone et al. 1985; Whitten et al. 1985).

Using toluene as an example, these mechanisms predict either the formation of three molecules of α-dicarbonyls for each molecule of toluene that undergoes ring opening [as predicted by the "recyclization" mechanism assumed by Killus and Whitten (1982), and incorporated into the latest Carbon Bond mechanism (Whitten et al. 1985)] or that one α-dicarbonyl molecule and one homologue to 2-butene-2,4-dial is formed [as predicted by the "cyclization" mechanism assumed in the mechanism of Atkinson et al. (1980, 1982), Atkinson and Lloyd (1984), Leone and Seinfeld (1984), and Leone et al. (1985)]. Both of these predictions are inconsistent with the recent α-dicarbonyl product yield data, which indicate that glyoxal and methylglyoxal account for only 35% of the ring-opening reaction route from toluene if the cyclization mechanism is assumed, and only 12% of the reaction if recyclization is assumed. In addition, the qualitative product studies of Shepson et al. (1984) and Dumdei and O'Brien (1984) indicate that 2-butene-1,4-dial, or its methyl-substituted analogues, 2-pentene-1,4-dial and 2-methyl-2-butene-1,4-dial (predicted to be formed from toluene by the cyclization mechanism) are not the only unsaturated ring-opening products. Indeed, these studies show that the actual toluene ring-opening reaction mechanism is much more complex than previously assumed.

The formation and reactions of these uncharacterized products cannot be ignored in the aromatic mechanism because doing so results in mechanisms that significantly and consistently underpredict the reactivity observed in aromatic hydrocarbon - NO_x - air environmental chamber experiments. This is particularly true for those experiments carried out in the SAPRC Indoor Teflon Chamber (ITC), whose blacklight light source is such that the α-dicarbonyls photolyze at significantly lower rates than is the case in the SAPRC Evacuable Chamber (EC) or in outdoor chambers. Indeed, the previous mechanisms that assumed high α-dicarbonyl yields, which could simulate toluene runs carried out in the SAPRC EC and outdoor chambers (e.g., Leone et al. 1985), significantly underpredict reactivity in toluene runs carried out in the ITC, due to the lower calculated methylglyoxal photolysis rate. However, because of the present lack of knowledge of the ring-opening reactions of aromatic hydrocarbons, and of the nature and reactions of the non-α-dicarbonyl products formed, no attempt was made in this mechanism to represent non-α-dicarbonyl products explicitly. Instead, non-α-dicarbonyl products were represented in a parameterized manner, as indicated below.

In the Phase I version of this mechanism, the uncharacterized, non-α-dicarbonyl ring-opened products were lumped together and represented as "aromatic unknowns" (one for each aromatic hydrocarbon), whose subsequent reactions were represented as being analogous to the reaction mechanisms previously proposed (Atkinson et al. 1980; Atkinson and Lloyd 1984) for the 1,4-unsaturated dicarbonyls that had been assumed to be the co-products to the α-dicarbonyls but modified to conserve carbon and the number of methyl groups. In order for the mechanism to simulate the observed reactivity of the aromatic hydrocarbons, each of these "unknowns" was assumed to photolyze to yield radicals, with the photolysis rate for "unknown" for each aromatic adjusted to fit the results of the single component aromatic - NO_x - air irradiations carried out in the SAPRC EC and the SAPRC ITC. In order for the same mechanism to successfully simulate experiments in both the EC and the ITC, which have significantly different spectral distributions, it was necessary to assume that the "unknowns" photolyze primarily by absorption of light in the wavelength region below 350 nm (significantly lower wavelengths than that are responsible for the photolysis of the α-dicarbonyls). It was also necessary to assume that the reactions of the "unknowns" with OH radicals result in the formation of PAN analogues, since not assuming this results in a consistent tendency for the mechanism to overpredict final ozone yields in aromatic - NO_x - air irradiations. These aromatic mechanisms, optimized based on fits to SAPRC EC and ITC runs, were found to give satisfactory simulations of toluene-NO_x and o-xylene-NO_x runs carried out in the University of North Carolina (UNC) outdoor chamber (Carter et al. 1986).

The Phase II aromatic photooxidation mechanism uses a somewhat different parameterization of the reactions of the aromatic ring-opening products. This alternative representation was selected because it could fit the environmental chamber data as well as and, in some cases better than, the Phase I mechanism and because it involved fewer species and reactions. In this representation, two separate species were used to represent the unknown non-α-dicarbonyl products instead of one for each aromatic. The PAN analogues formed from the unknown products were lumped with PAN analogues formed in other areas of the mechanism, specifically those formed from the reactions of glyoxal and "RCHO", the lumped higher aldehyde. The specific set of reactions assigned for each was chosen to be analogous for those for the α-dicarbonyls, rather than the 1,4-unsaturated dicarbonyls as used in the previous representation of the unknown products. The photolysis rates and yields of these "lumped aromatic unknown products" in the photooxidations of benzene, toluene, m-xylene, and 1,3,5-trimethylbenzene were adjusted to obtain best fits to the results of selected aromatic - NO_x - air irradiations carried out in the SAPRC EC and ITC, using a non-linear least squares optimization program. As was the case with the previous representation, in order to fit reactivity in EC and ITC experiments with the same mechanism, the products were assumed to photolyze in the 290 - 350 nm wavelength region. The data were adequately fit by assigning one of the unknown products (BGLY) to represent the unknowns formed from benzene, and the other unknown product (DIAL) to represent the unknowns from the methylbenzenes, with DIAL photolyzing 13.3 times faster than BGLY. This parameterized mechanism simulated the aromatic - NO_x - air experiments as well as, and in some cases better than, the alkene and alkane mechanisms that simulated comparable single component experiments (see Section 2.2). Overall, the Phase II aromatic mechanism is slightly slower in oxidizing NO_x than the Phase I aromatic mechanism. In light of its good performance, it is difficult to justify using a more complex aromatic mechanism until better data become available.

Lastly, the Phase II mechanism only uses propionaldehyde and methylethylketone (MEK) to represent the bi- and poly-functional products formed in the photooxidation of alkanes (depending on whether the product has aldehyde or ketone groups). In the Phase I mechanism, a propionaldehyde, MEK, and pentanol were used to represent these bi- and polyfunctional products. Thus, the pentanol reactions have been eliminated from the mechanism. This change has virtually no effect on the mechanism's predictions for key species such as NO, NO_2, O_3, and alkanes.

2.2 Evaluation Results

The results of evaluation using the Phase II detailed mechanism are summarized in this section. The performance measures employed in the evaluation are the relative and absolute errors in the maximum ozone concentrations and the NO_x oxidation rate. The NO_x oxidation rate is assessed using the average rate of change of ozone minus NO [ie., d([O3]-[NO])/dt in ppb/minute] during the first half of the period required to reach ozone maximum. This measure of NO_x oxidation rate is preferred over time to reach 50% of the [O3]-[NO] maximum, used in the Phase I evaluation, because there is much less disparity in the values of the rates for different chambers with this approach. Other measures of model performance include the relative and absolute errors in the maximum PAN and aldehyde concentration and in the half-lives of the organic precursors. The performance measures for each experiment simulated in the evaluation are listed in Appendix A of this report.

The protocol used to test the chemical mechanism incorporates several unique elements. First, where practical, all reactants in the experiments were represented by explicit chemical reactions in the mechanism. For example, simulations of n-octane/NO_x experiments were performed with the n-octane mechanism rather than the lumped C6+ alkane mechanism. The major exception to this was the auto exhaust simulations, which have too many species for this approach to be feasible. Second, a consistent set of assumptions was used in modeling all runs. Run-to-run adjustments of uncertain parameters to optimize fits to the data were not allowed. Adjustments of mechanistic and chamber effects parameters were developed using only the most appropriate runs for the particular parameter and were then incorporated on a global basis into the testing program. Third, poorly understood chamber effects were represented as simply as possible in order to avoid introducing additional uncertain parameters. The minimum number of parameters needed to describe the data were incorporated into the parameterizations. Fourth, and very important, a large number of runs were used to evaluate the performance of the mechanism. Only runs that had major gaps in critical input data were eliminated from the testing data base. The use of a large number of runs is important because, now that the mechanism has been applied to many experiments, it is clear that there is considerable inherent variability in the environmental chamber data. Thus, performance information that is based on simulating a small number of runs or only runs from one chamber may be misleading. Fortunately, there is a large number of experiments for propene, toluene, n-butane, and surrogate mixtures that can be used to reliably evaluate the mechanism.

The evaluation was performed using environmental chamber data from four facilities:

- SAPRC 5800-liter Indoor Evacuable Chamber (EC)
- SAPRC 6400-liter Indoor Teflon Chamber (ITC)
- SAPRC 50,000-liter Outdoor Teflon Chamber (OTC)
- UNC 30,000-liter Outdoor Teflon Chamber (UNC)

The number and type of chamber runs used in the evaluation are summarized in Table 2-6. The table shows that 491 experiments were used in the testing. About 175 of the experiments employed complex mixtures that were surrogates for the organics found in urban atmospheres.

The evaluation was carried out in three steps. The first step involved modeling chamber characterization experiments to estimate the chamber effect parameters. Pure air, NO_x-air, NO_x-CO-air, formaldehyde-air, and acetaldehyde-air experiments were used in this step. The second step involved modeling single organic - NO_x experiments to test and refine the mechanisms for the organic precursors in the mechanism. The third step involved modeling organic mixtures in the presence of NO_x. No adjustments of the mechanism were made at this step. The synthetic mixtures were subdivided into simple and complex mixtures, where the simple mixtures have species from one or two of the three major classes of organics and the complex mixtures have species from all three major classes of organics. Simulations of auto exhaust experiments and dynamic

TABLE 2-6

SUMMARY OF ENVIRONMENTAL CHAMBER RUNS USED FOR MECHANISM EVALUATION

Type of Environmental Chamber Run		Number of Runs				
		EC	ITC	OTC	UNC	Total
Characterization	Various	10	14	10	37	71
Single Organic-NO_x	Oxygenates	7	1	2	15	25
	Ethene	6	2		6	14
	Propene	15	7	5	22	49
	Butenes	6	5		5	16
	n-Butane	14	5	1	7	27
	>C4 Alkanes	6	8		6	20
	Toluene	13	2		5	20
	Other Aromatics	7	13		4	24
Known Mixtures	Simple Mixtures	22			18	40
	Complex Mixtures	11	45	62	33	151
Auto Exhaust	Two Vehicles				25	25
Dynamic Injection	Propene and Mixtures				9	9
Total Number of Runs		117	102	80	192	491

injection experiments were also included in the testing, as described in Carter et al. (1986).

Although higher quantum yields for NO_2 are used with the Phase II detailed mechanism, the Phase I and II evaluations were performed with identical NO_2 photolysis rates. The reason for this is that the NO_2 photolysis rates are considered part of the experimental data base. However, because the theoretical NO_2 photolysis rates are higher, the ratios of the photolysis rates of other species to the NO_2 photolysis rate were lower in the Phase II evaluation. Overall, this change slightly improved fits of the predictions to the experimental data.

The model performance in the NO_x-air and NO_x-CO-air simulations is shown in Figure 2-1. The predicted and observed change in [NO] and [NO_2] concentrations over the course of the runs is shown in the figure. These are the best measures of performance because very little ozone is formed in these high NO_x characterization runs. The figure shows that agreement for the change in NO and NO_2 concentrations is within about ±20% for all of the cases.

The predicted and observed maximum ozone concentrations and d([O3]-[NO])/dt are shown in Figures 2-2 through 2-5 for the single oxygenate, alkene, alkane, and aromatic simulations, respectively. Examples of the distribution of errors in maximum ozone and the timing parameter for propene, n-butane, and toluene are shown in Figures 2-6 and 2-7. The results for the oxygenates, alkenes and aromatics show that the maximum ozone and timing parameter predictions are within ±30% of the observed in almost all cases. The distribution of errors for propene and toluene shows that the errors are somewhat normally distributed about zero error. This level of agreement is considered quite good. The results for the alkane simulations show a large amount of scatter and indicate unsatisfactory model performance. The alkanes are the least reactive compounds in the mechanism and the simulations of their oxidation are very sensitive to the chamber characterization procedures, particularly the rate of radical off-gassing from the chamber walls. The uncertainty in the chamber effects makes it almost impossible to evaluate the alkane mechanism without ambiguity at this time.

The predicted and observed maximum ozone concentrations and d([O3]-[NO])/dt are shown in Figures 2-8 through 2-10 for the simple

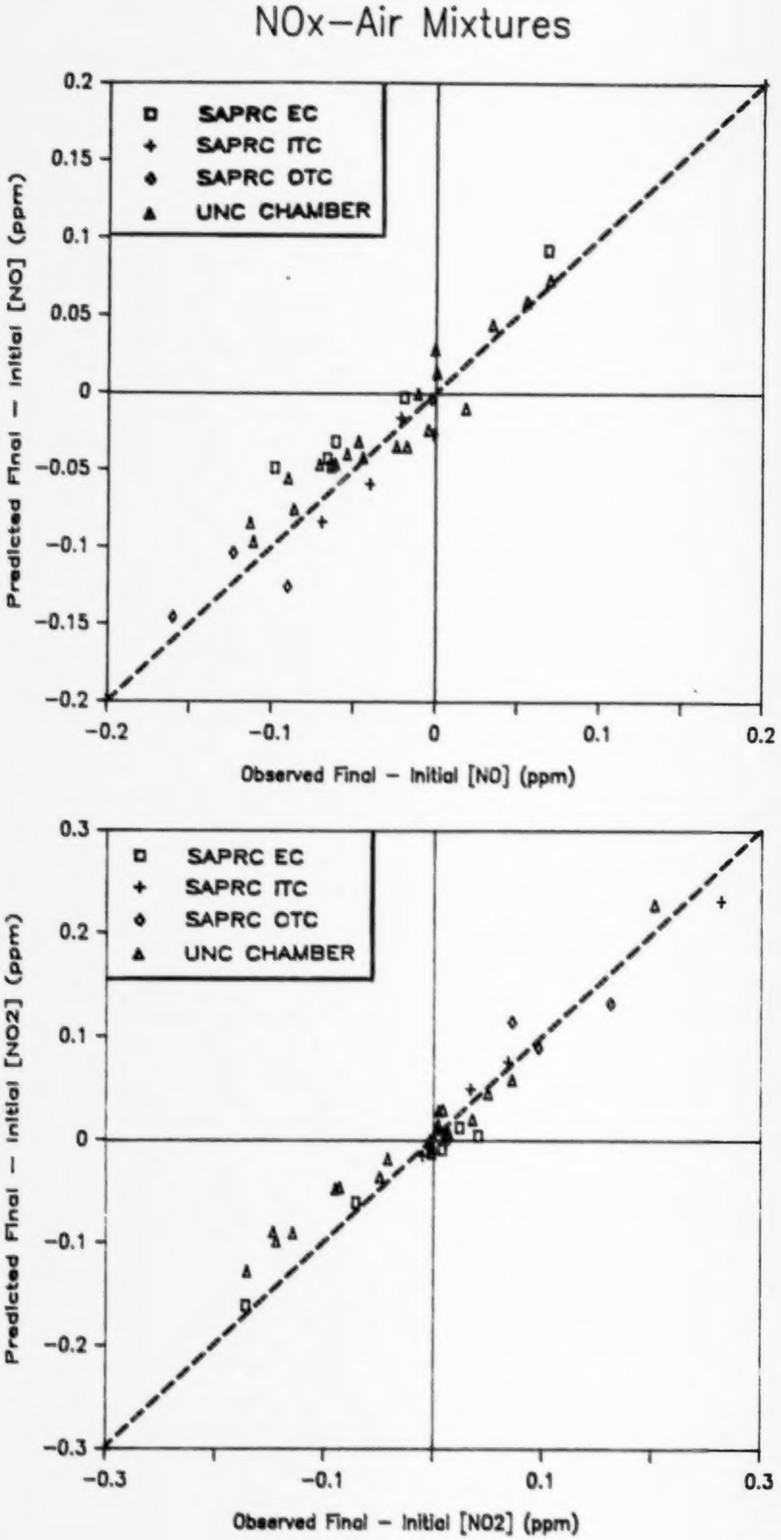

Figure 2-1. Predicted versus observed change in NO and NO_2 for NO_x-air and NO_x-CO-air characterization runs.

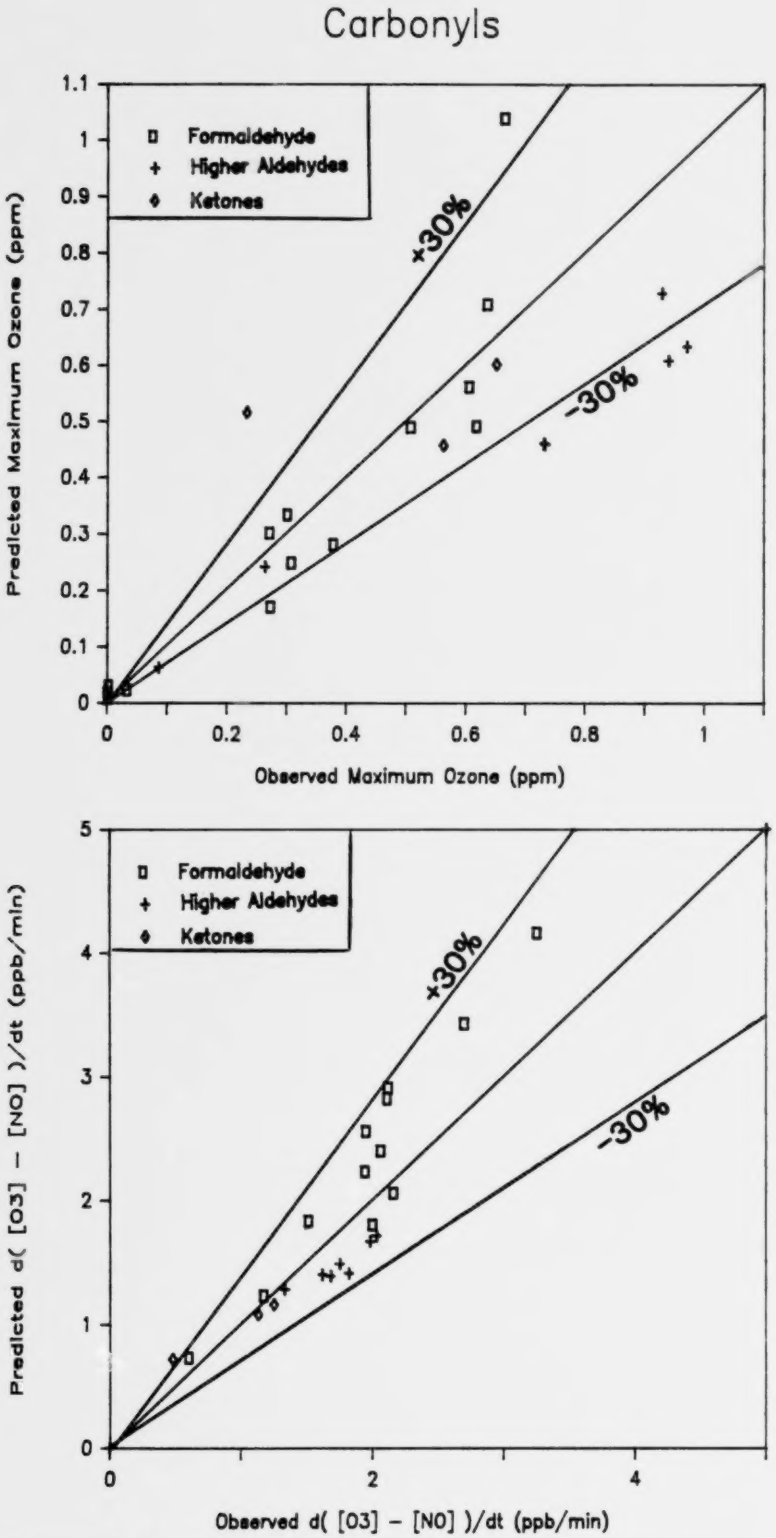

Figure 2-2. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for carbonyl-NO_x runs.

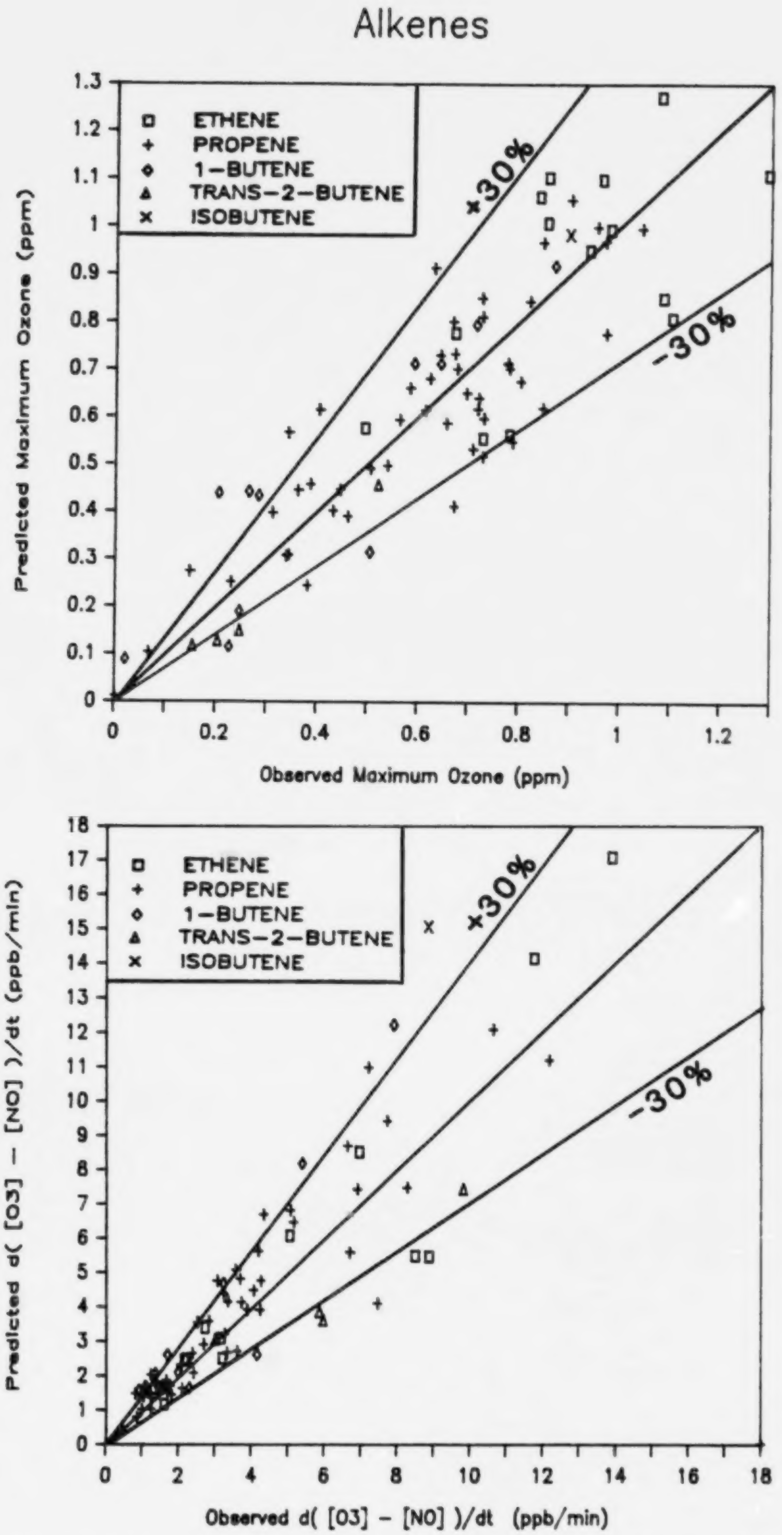

Figure 2-3. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for alkene-NO_x runs.

Alkanes

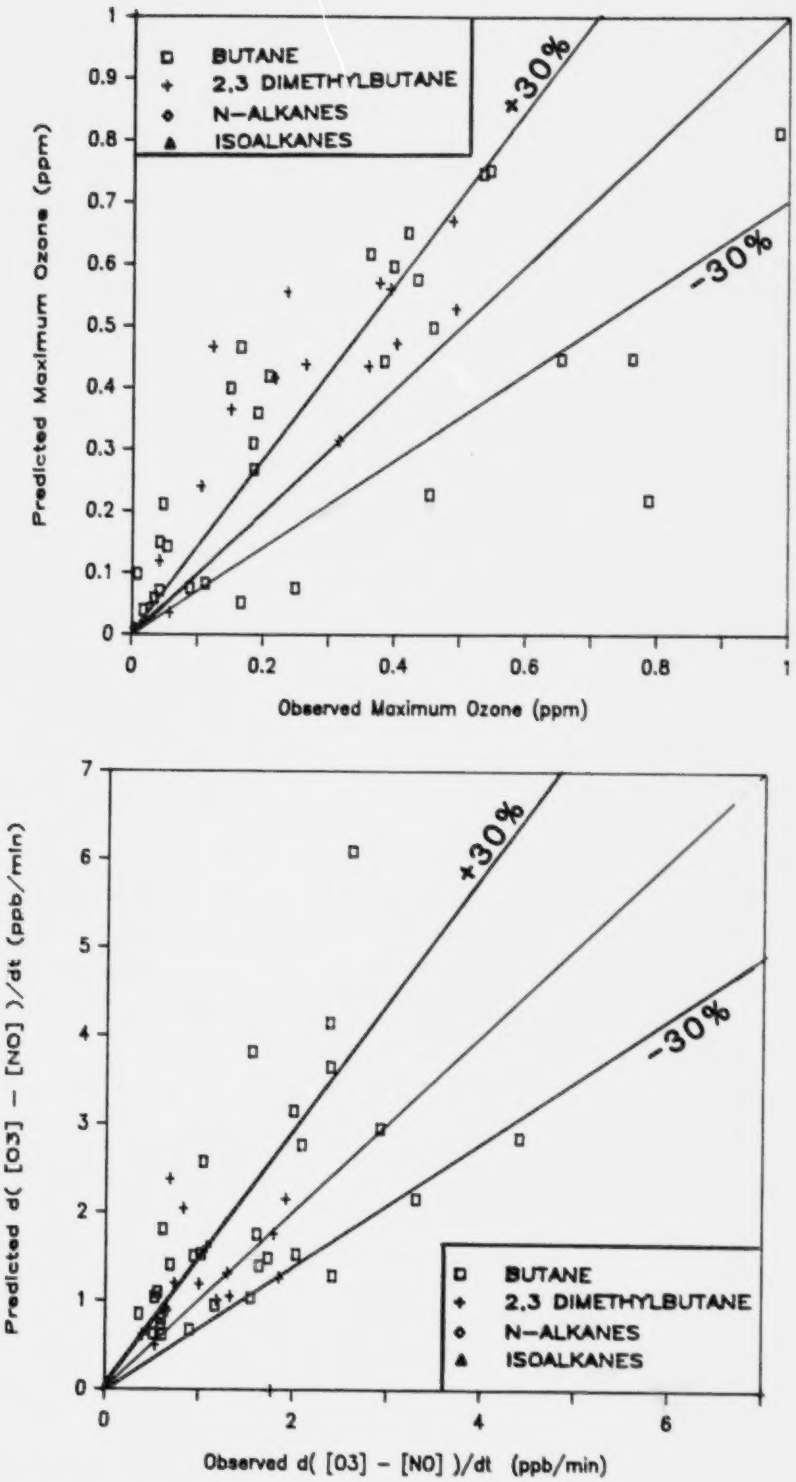

Figure 2-4. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for alkane-NO_x runs.

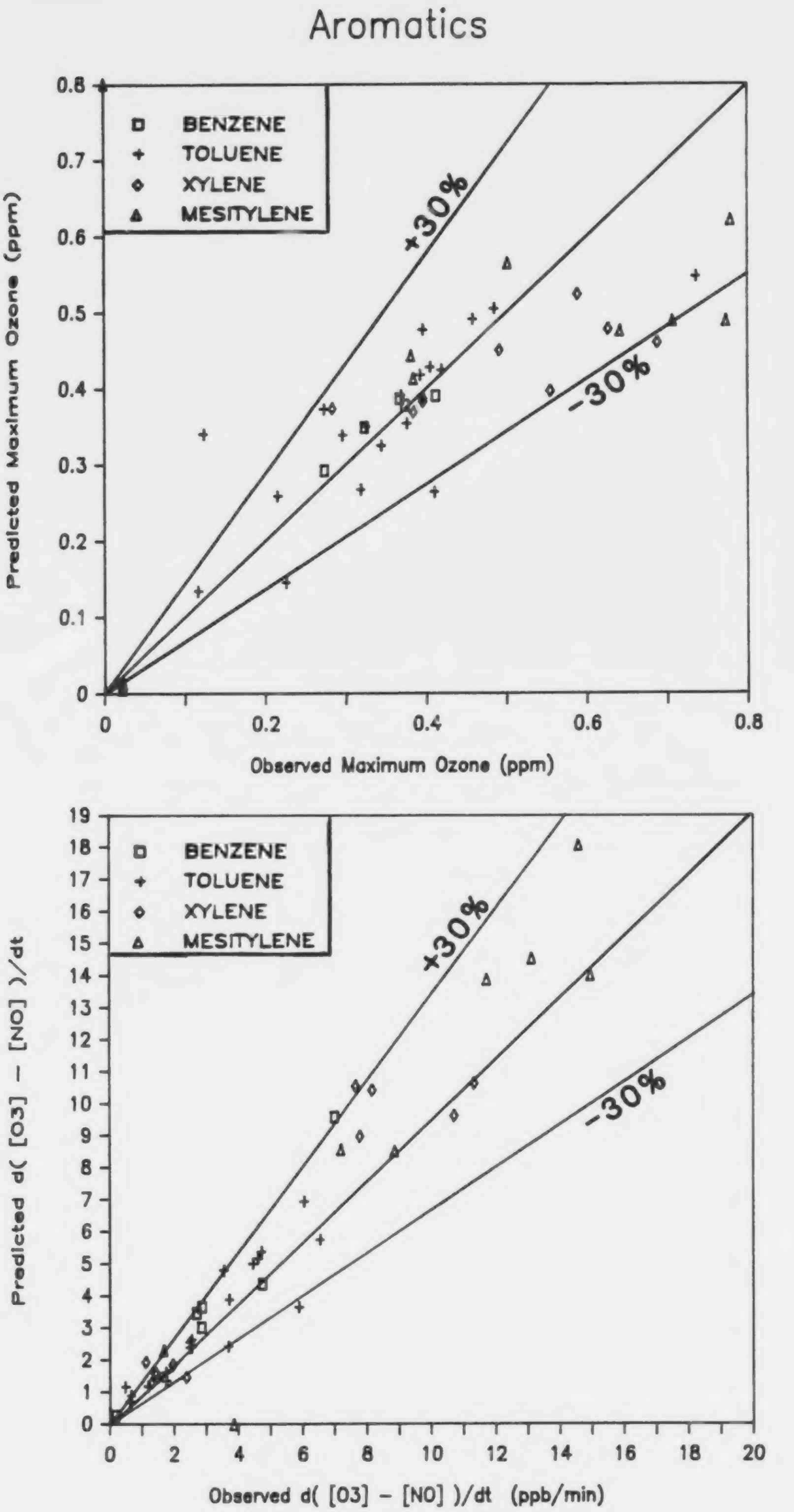

Figure 2-5. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for aromatic-NO_x runs

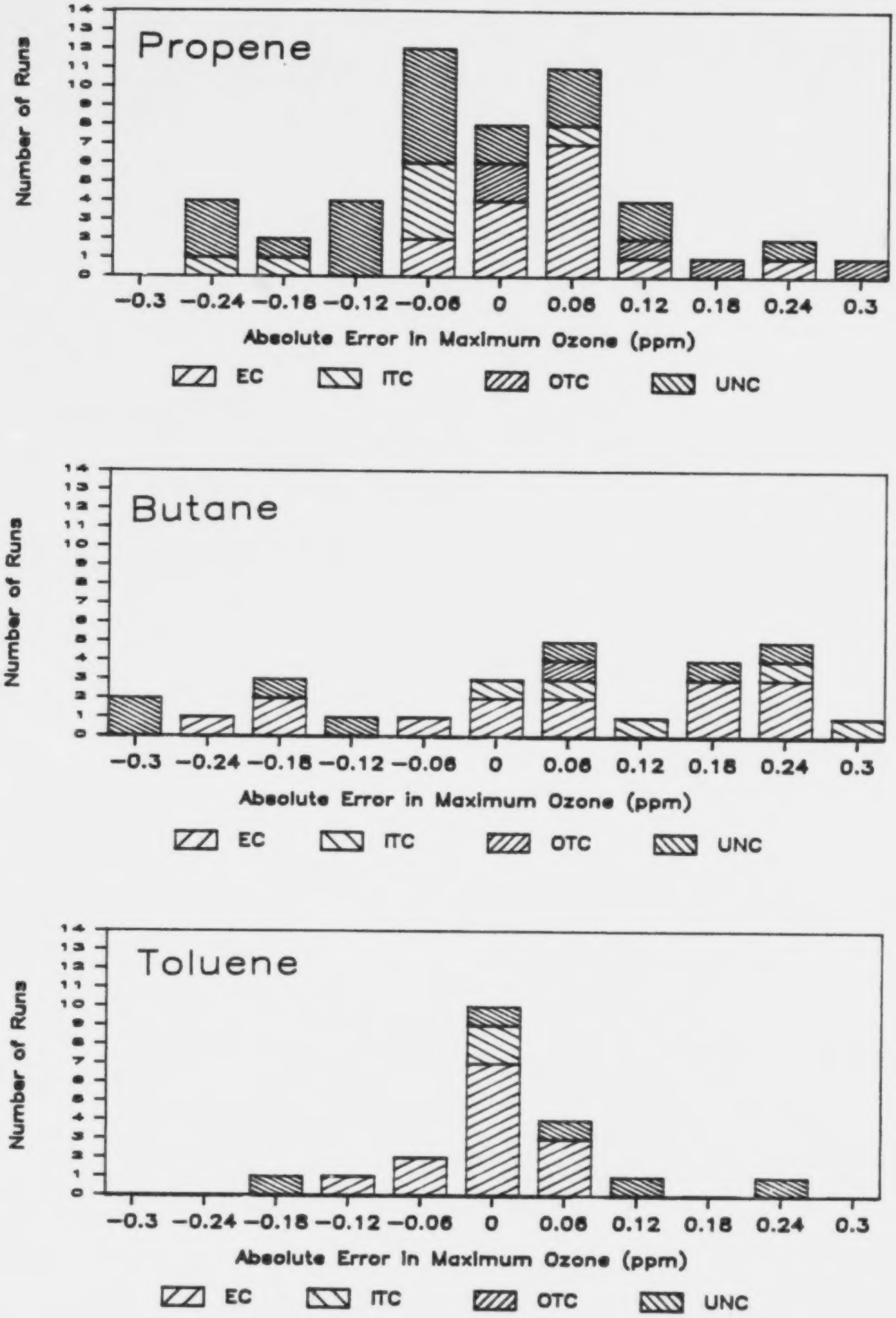

Figure 2-6. Distributions of absolute error in maximum ozone predictions for propene, n-butane, and toluene runs.

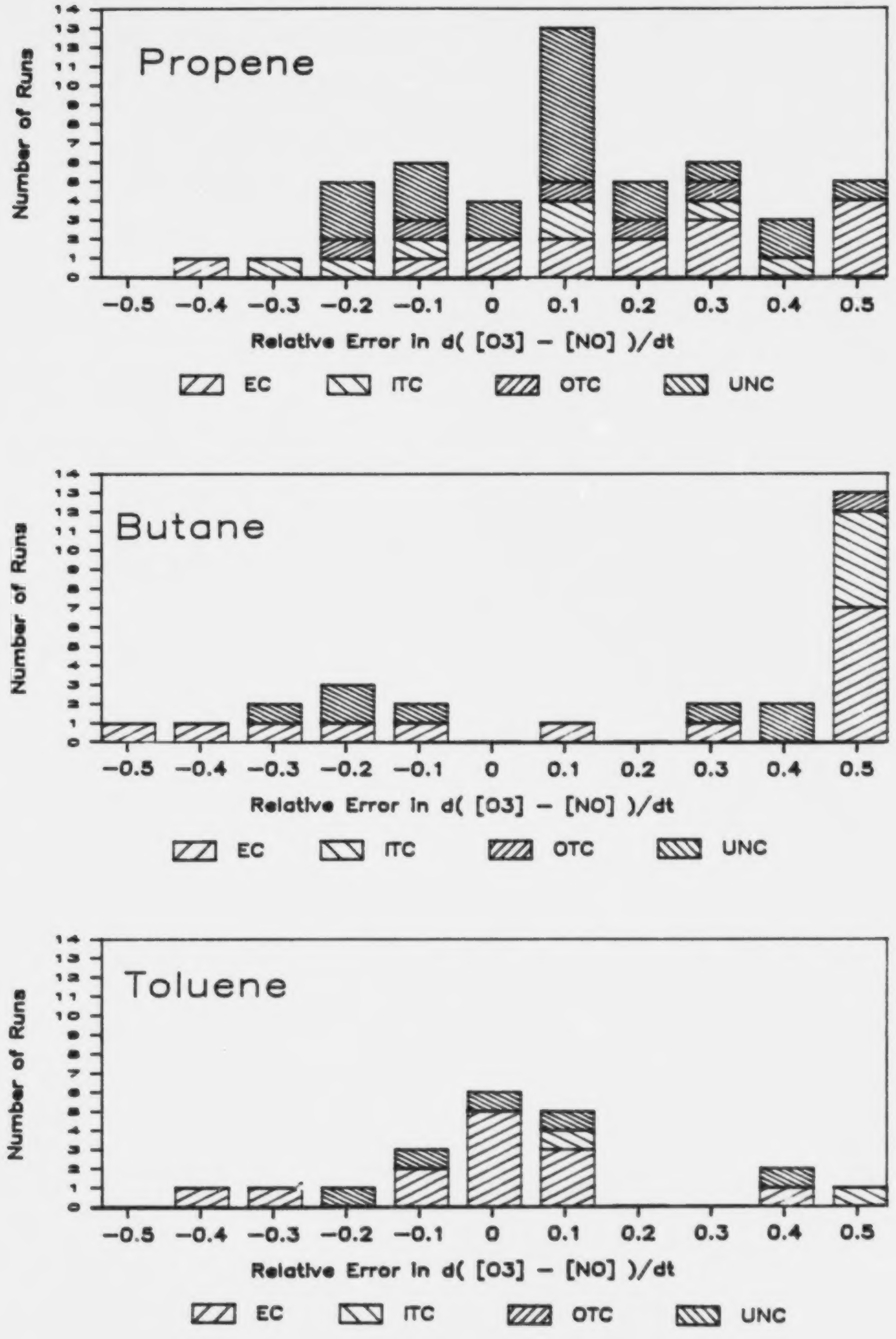

Figure 2-7. Distributions of relative errors in d([O_3]-[NO])/dt for propene, n-butane, and toluene runs.

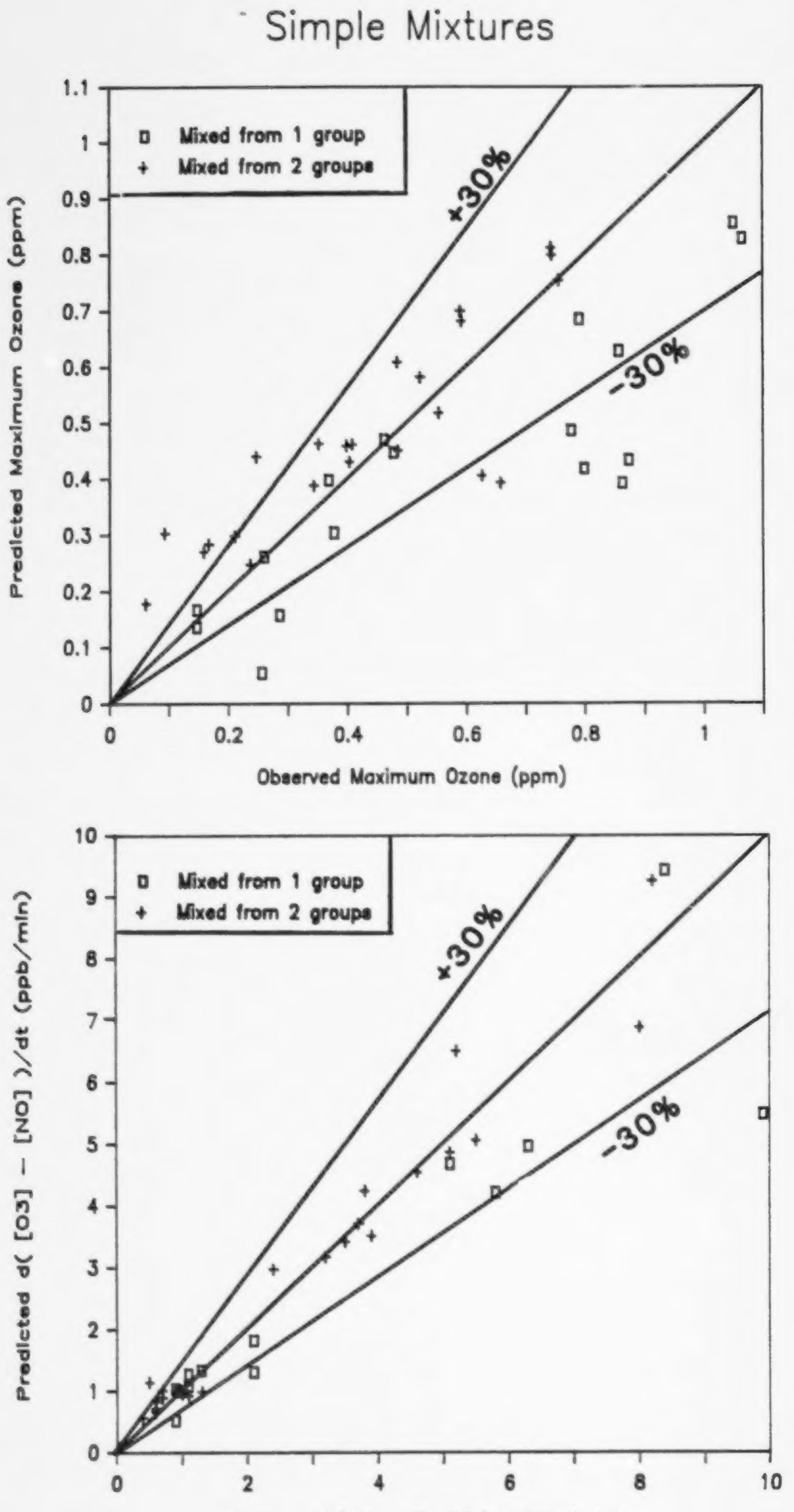

Figure 2-8. Predicted versus observed maximum ozone and d($[O_3]$-[NO])/dt for simple organic mixture runs.

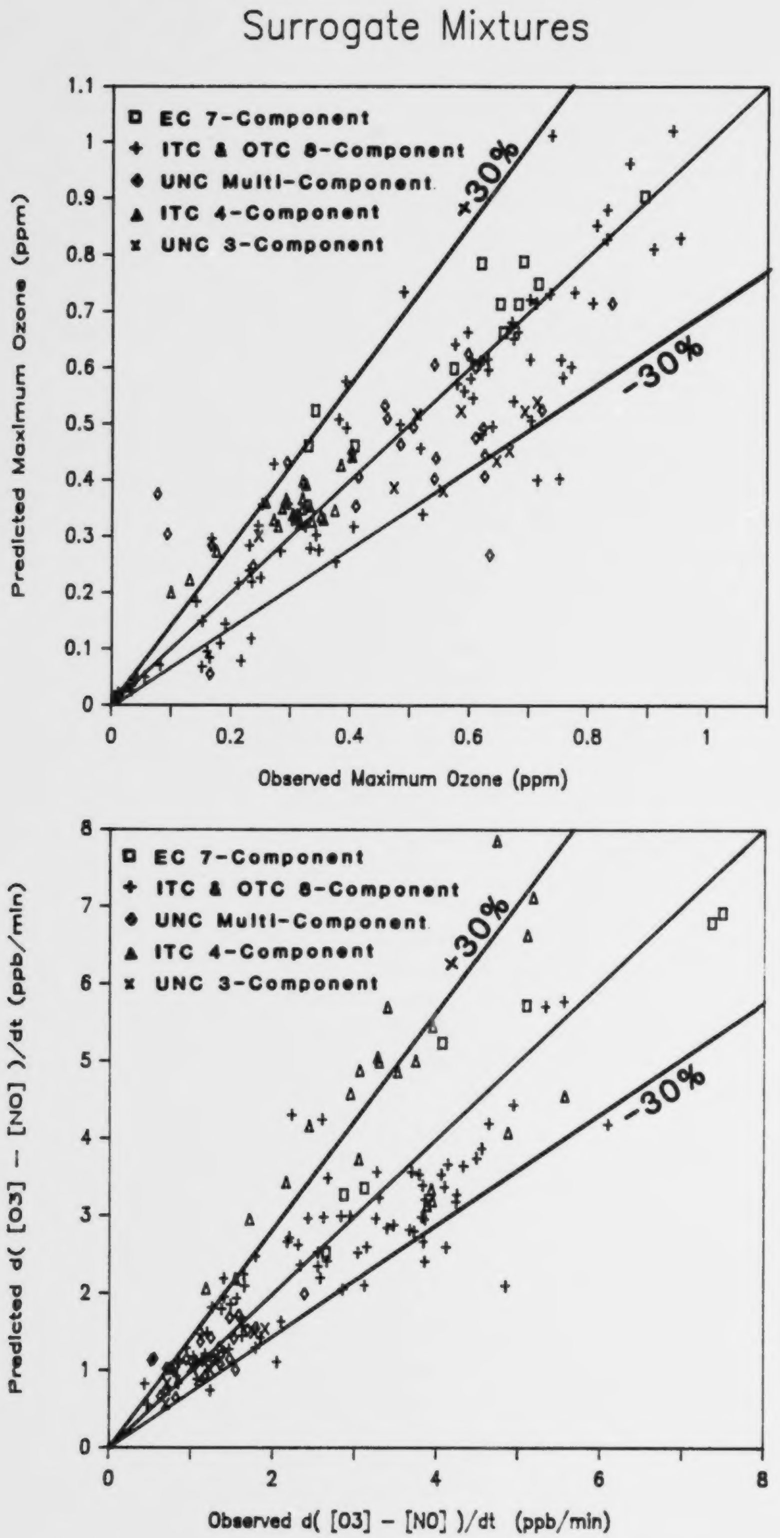

Figure 2-9. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for surrogate mixture runs.

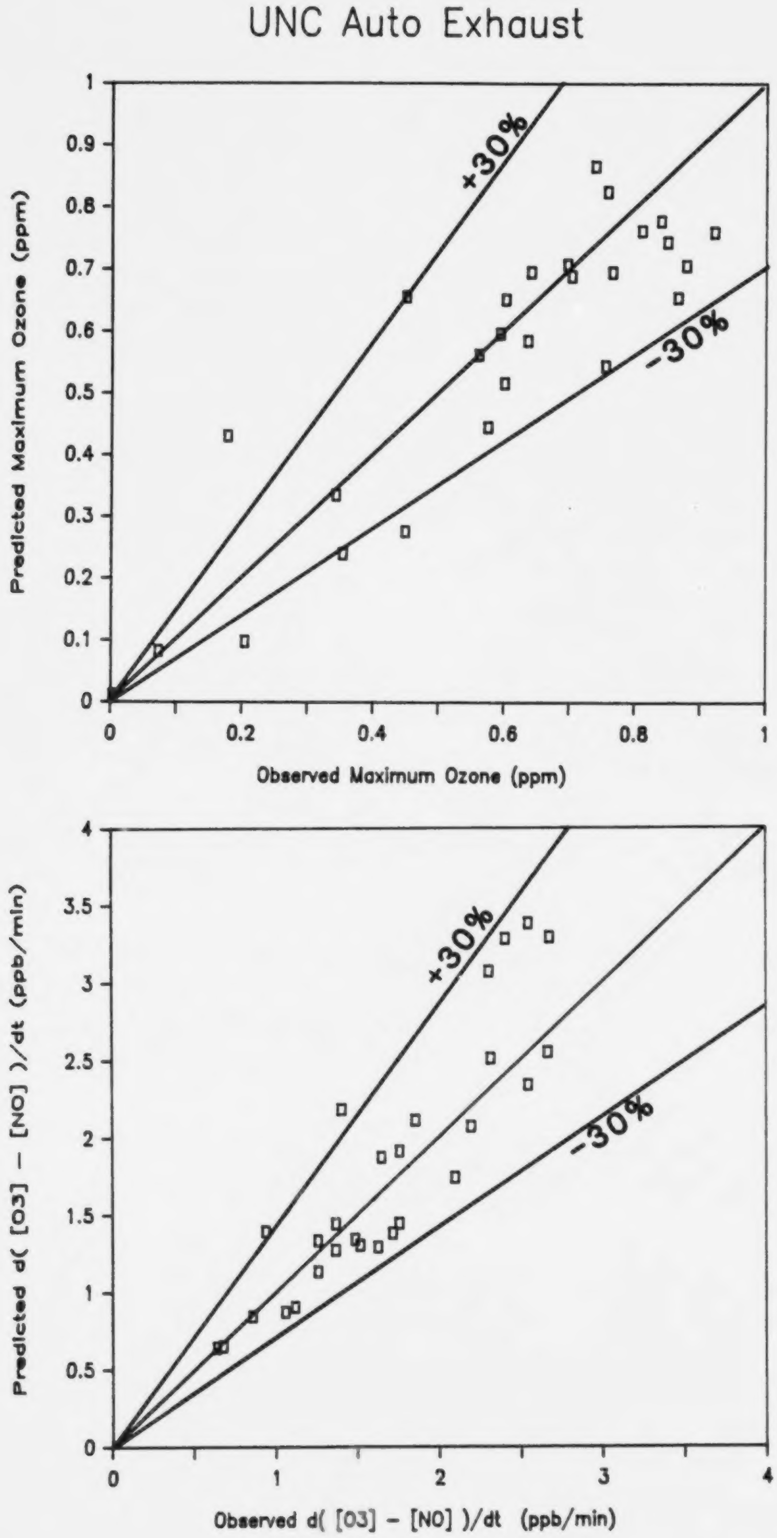

Figure 2-10. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for UNC automobile exhaust runs.

synthetic mixtures, complex surrogate mixtures, and the auto exhaust irradiations. The distribution of errors in the ozone maxima and timing parameter is shown in Figures 2-11 and 2-12. The results for the simple mixtures show that most of the maximum ozone predictions agree with the observed values within ±30%. However, there are several mixed alkene runs from the EC that show greater than 30% underprediction of the ozone yield. The results for the complex surrogate mixtures show the vast majority of runs have better than ±30% agreement on the maximum ozone concentrations and the timing parameter. The distribution of errors in the ozone is centered on zero and shows roughly equal numbers of over- and under-predictions. Similarly good performance is shown for the auto exhaust experiment simulations.

The average bias and error in the mechanism's ozone predictions for these experiments are shown in Table 2-7. These data show that the average bias and error in the oxygenate simulations is -5% and ±25%, respectively. The performance for formaldehyde runs is considerably better than for higher aldehydes and ketones. The average bias and error for ozone in the alkene simulations is +3% and ±21%, respectively. The performance for ethene and propene is quite good; the performance for butenes is adequate. The average bias and error for the alkane runs are +46% and ±69%, respectively. The performance on n-butane experiments is better than this, but the performance on long-chain alkane experiments is much worse. These poor statistics reflect the previously discussed difficulties in testing the alkane mechanism. The average bias and error for the single aromatic runs are surprisingly small, +1% and ±19%, respectively. This good performance reflects the fact that the mechanism was optimized to fit most of the data. The statistics indicate that the toluene mechanism has a tendency to overpredict ozone, whereas the m-xylene and mesitylene mechanisms have tendencies to underpredict ozone yields on the average. Overall, for all single organic-NO_x runs, the mechanism overpredicts by 12% and the average error is ±33%.

The average bias and error for the simulations of mixtures indicate reasonably good model performance. The results for the simple mixtures show +10% bias and ±35%. The results for the mini- and full-surrogate complex mixtures are better, since the average error is only ±23%. For the auto exhaust runs, the average bias is -11% and the average error is

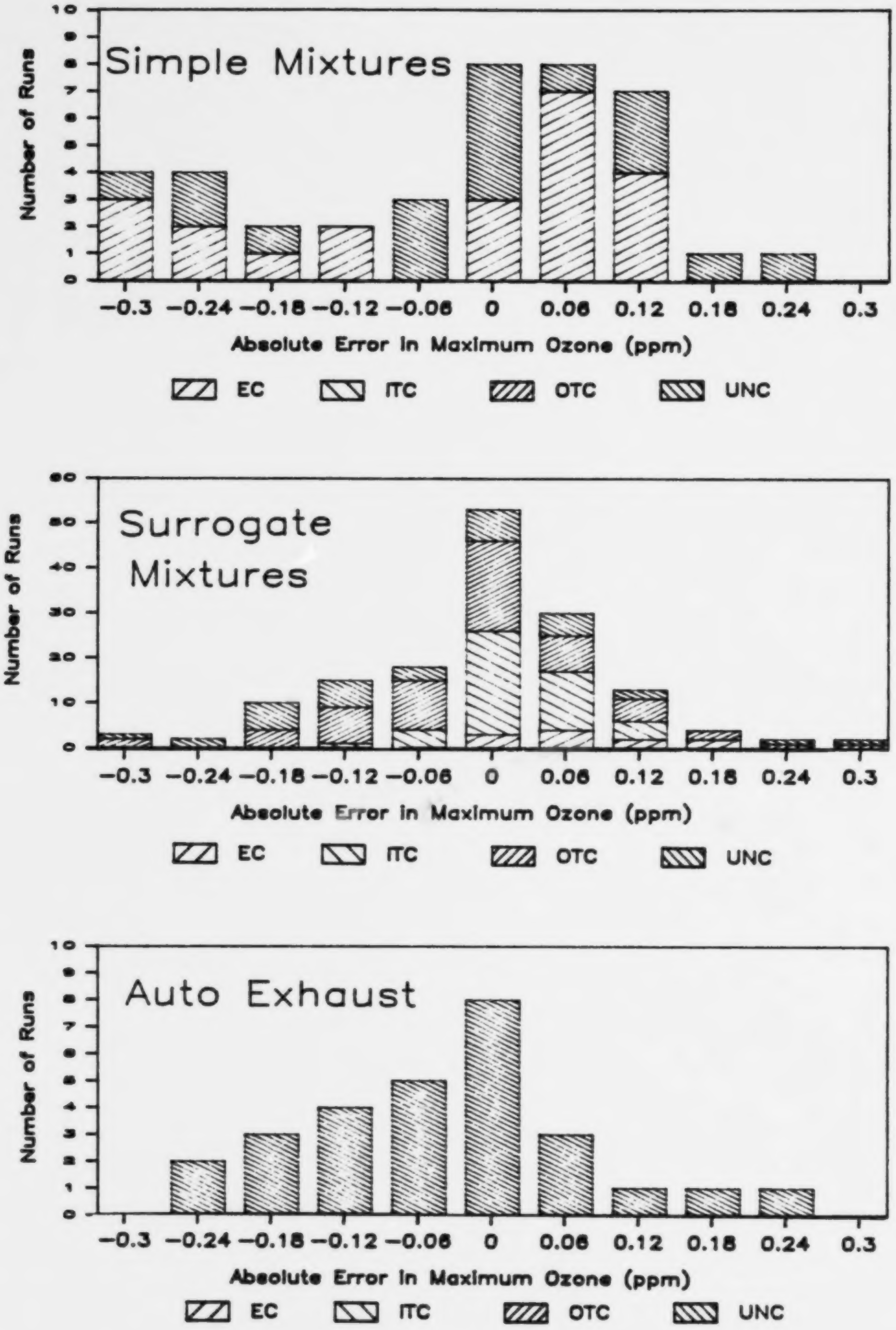

Figure 2-11. Distribution of absolute errors in maximum ozone predictions for simple mixtures, surrogate mixtures, and auto exhaust runs.

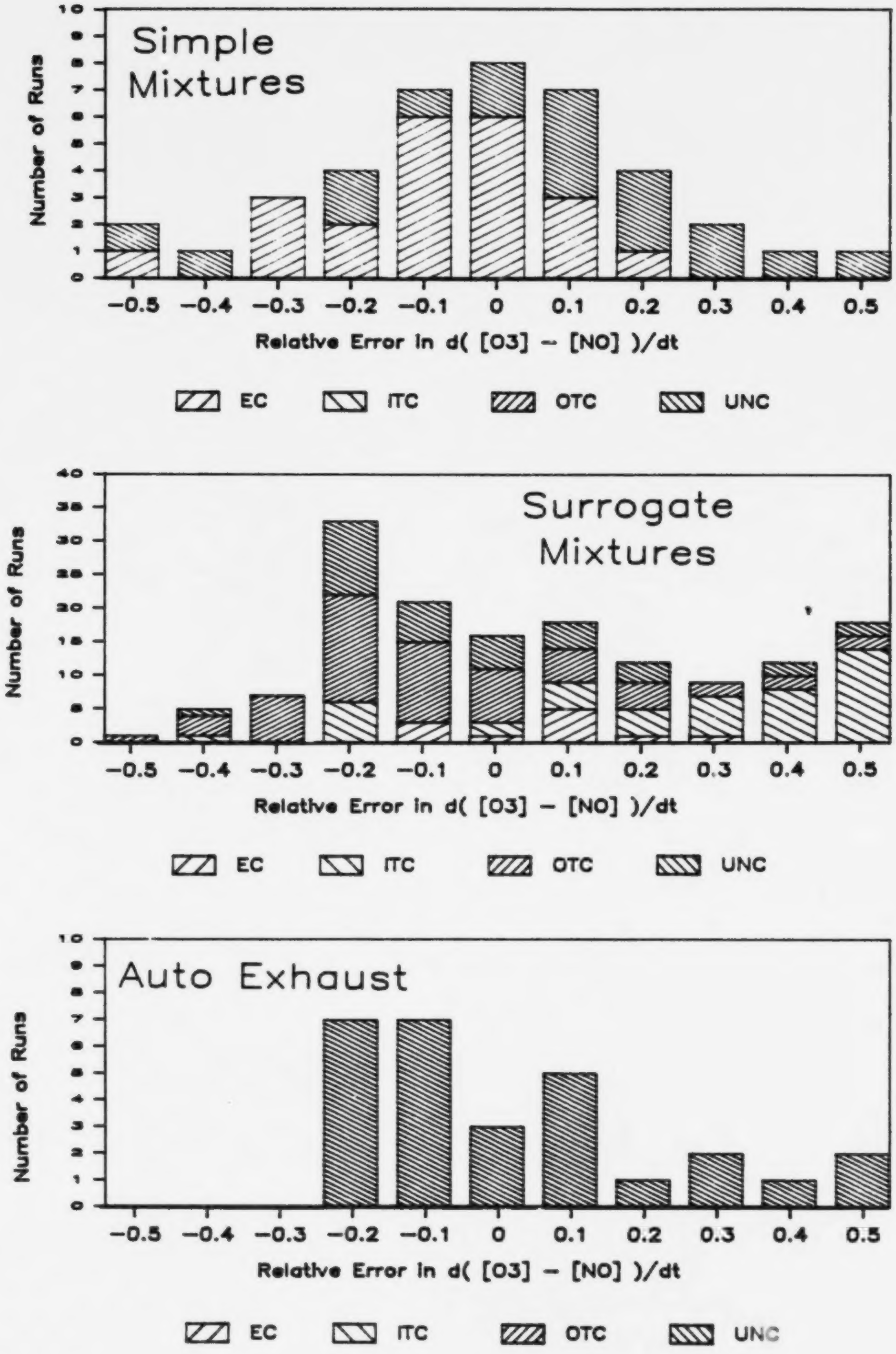

Figure 2-12. Distribution of relative errors in d([O_3]-[NO])/dt for simple mixtures, surrogate mixtures, and auto exhaust runs.

TABLE 2-7

AVERAGE MODEL PERFORMANCE FOR MAXIMUM OZONE

Run Type	Bias (%)	Error (%)
Formaldehyde	-1	19
Acetaldehyde	-26	26
Other Carbonyls	+4	44
All Carbonyls	-5	25
Ethene	+2	18
Propene	+3	18
Butenes	+4	34
All Alkenes	+3	21
Butane	+31	67
Branched Alkanes	+34	49
Long-chain Alkanes	+83	84
All Alkanes	+46	69
Benzene	+3	5
Toluene	+11	24
Xylenes	-9	16
Mesitylene	-11	21
All Aromatics	+1	19
All Single HC Runs	+12	33
Simple Mixtures	+10	35
Mini Surrogates	+10	22
Full Surrogates	+3	23
Auto Exhaust	-11	15
All HC Mixtures	+4	24
All Run Average	+7	28

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*Positive bias indicates model overprediction.

±15%. This is the smallest average error of all the groups, which is rather ironic since speciation of the organics in the auto exhaust runs was the least certain of any group of experiments in the data base. Overall, for all organic mixture simulations the performance statistics indicate that the mechanism overpredicts ozone maxima by 4% and the average error in the predictions is ±24%. Given the kinetic and mechanistic uncertainties, as well as chamber characterization uncertainties, this level of performance is quite satisfactory.

Another important aspect of the evaluation consisted of searching for systematic biases in the mechanism. The error in the ozone was plotted against the NO_x, NMOC, and NMOC/NO_x to investigate potential systematic errors. An example that shows the error in the surrogate mixture runs versus the log of the NMOC/NO_x ratio is illustrated in Figure 2-13. The distribution of errors appears to be fairly random for most of the range of NMOC/NO_x ratio for which there are experimental data. The errors are totally random for NMOC/NO_x ratios between 3 and 30. This indicates that there is no apparent relationship between the error in the prediction and this important ratio for the range of initial NMOC/NO_x ratios commonly occurring in ambient air. However, above a NMOC/NO_x ratio of 30, the mechanism tends to overpredict maximum ozone by a small amount in most cases. This small bias is not considered significant since all of the high NMOC/NO_x ratio runs are from one chamber.

The mechanism's predictive abilities for PAN and aldehydes were also examined in the evaluation. Figure 2-14 shows the predicted and observed PAN concentrations in the surrogate mixture runs. Only about half of the predicted PAN maxima are within ±30% of the observed PAN maxima. Figures 2-15 and 2-16 show the relative error in the PAN maxima for the propene, n-butane, toluene, simple mixture, complex surrogate mixture, and auto exhaust runs. The figures show fairly broad distribution of errors for all of the runs. Thus, the mechanism's predictions for PAN are clearly less accurate than its predictions for ozone. Figure 2-17 shows the distribution of the relative errors in the maximum formaldehyde concentrations for the propene, simple mixture, and complex surrogate mixture runs. These distributions indicate fairly poor fits between the mechanism and the data. In this case, the discrepancies probably reflect

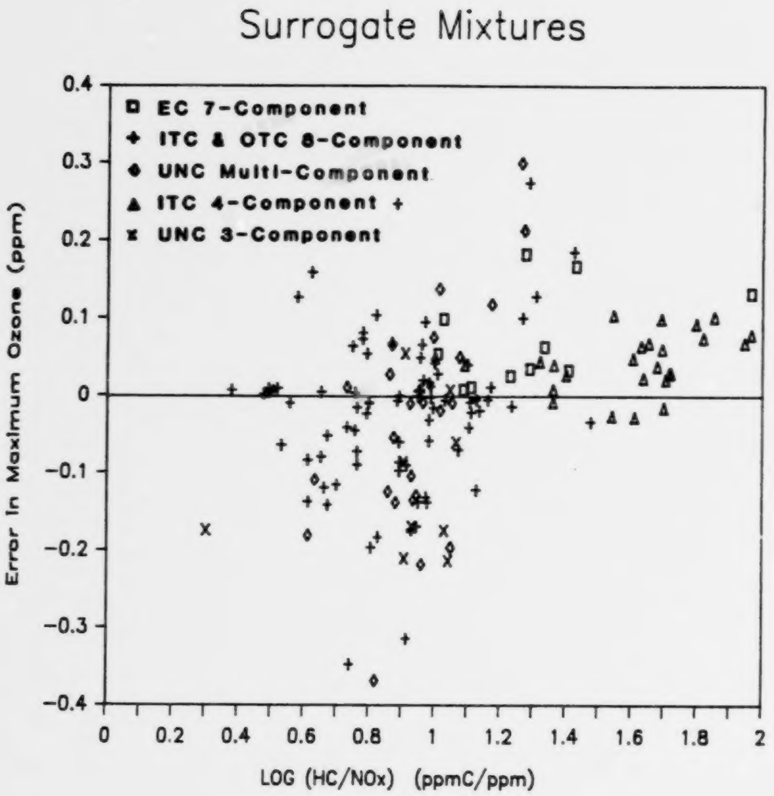


Figure 2-13. Absolute error in maximum ozone versus $\log_{10}$ ($NMOC/NO_x$)

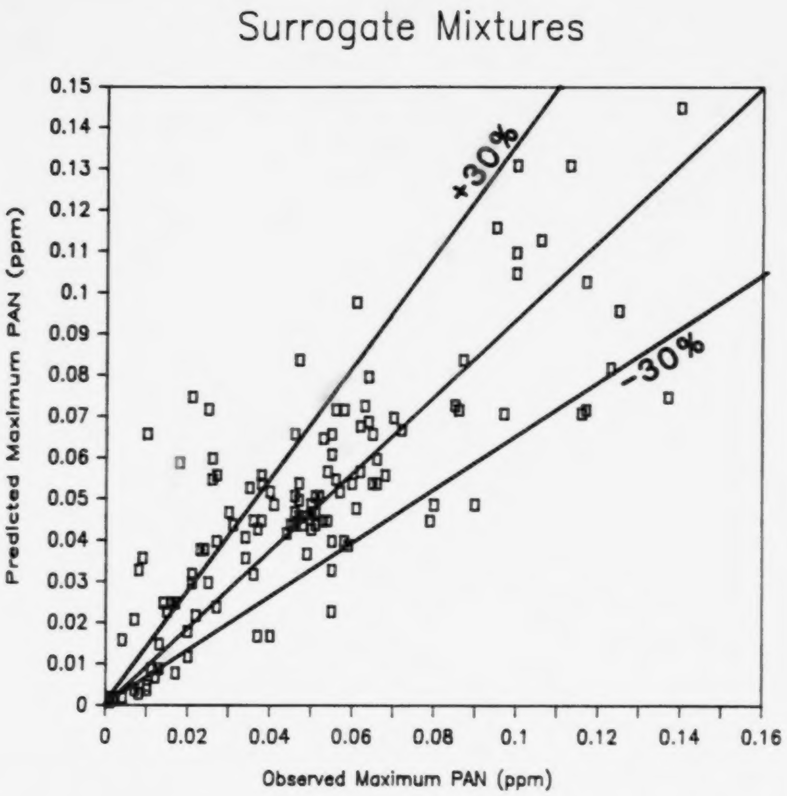


Figure 2-14. Predicted versus observed maximum PAN concentrations for surrogate mixture runs.

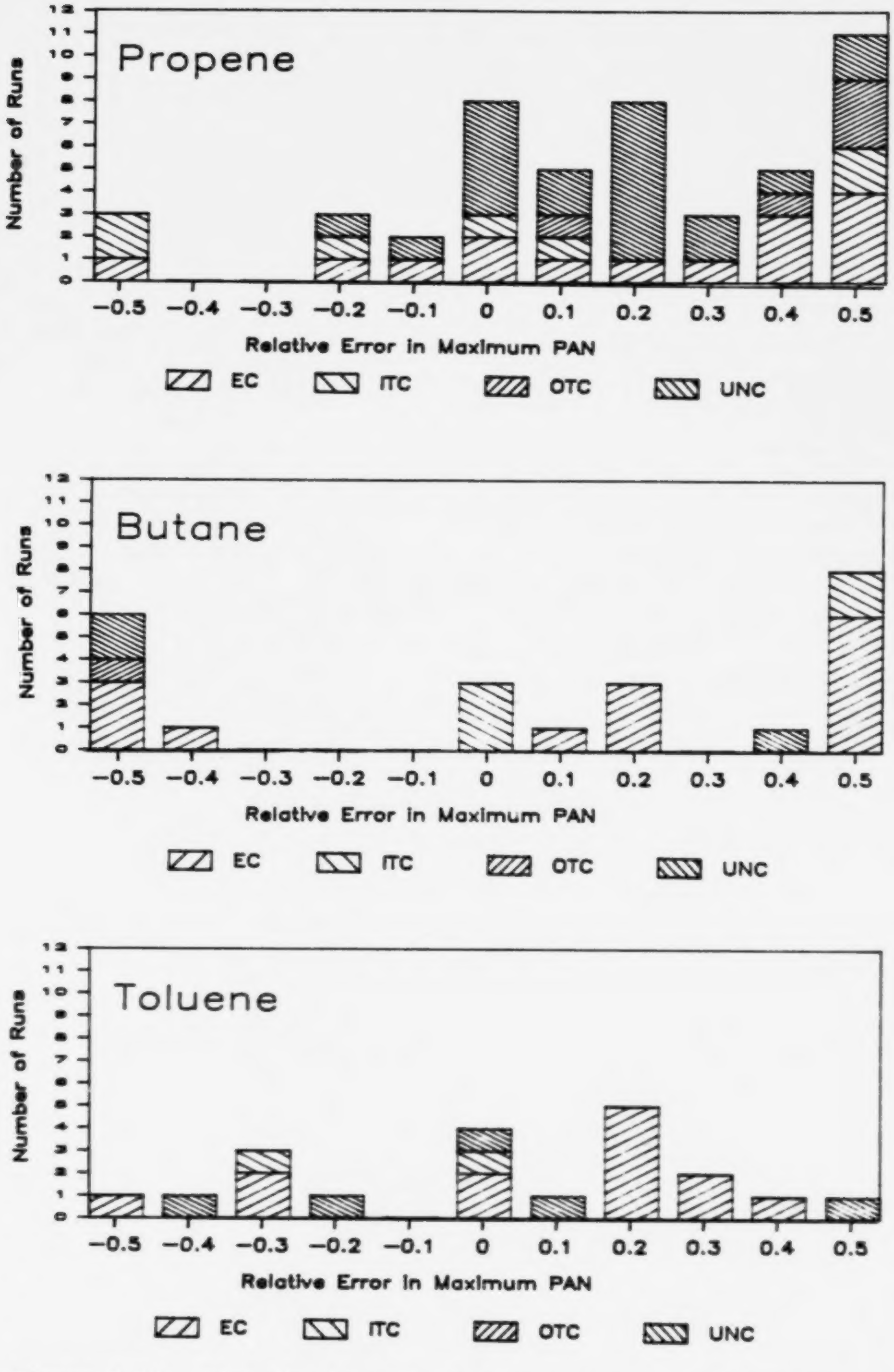


Figure 2-15. Distribution of relative errors in maximum PAN concentrations for propene, n-butane, and toluene runs.

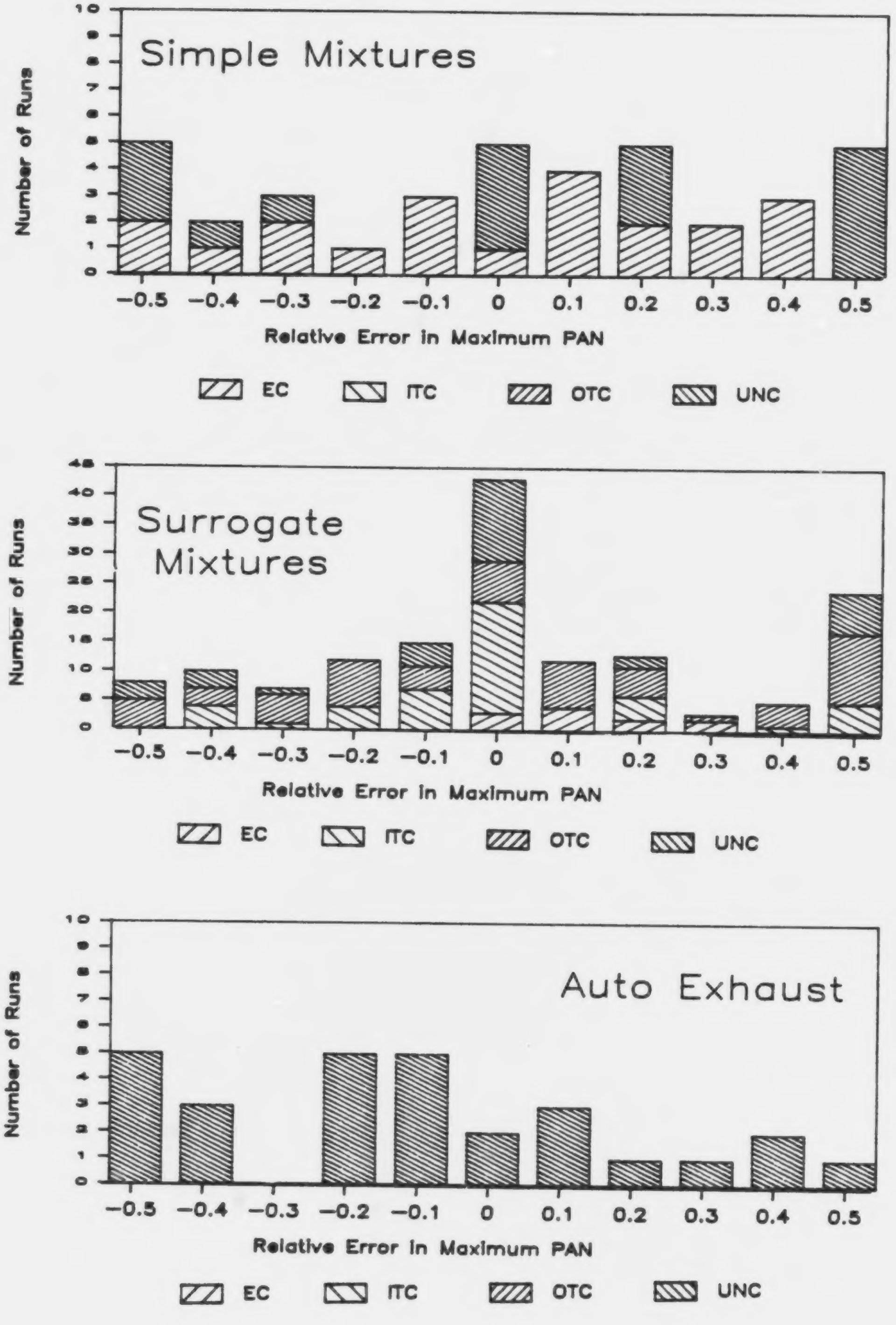


Figure 2-16. Distribution of relative errors in maximum PAN concentrations for simple mixture, surrogate mixture, and auto exhaust runs.

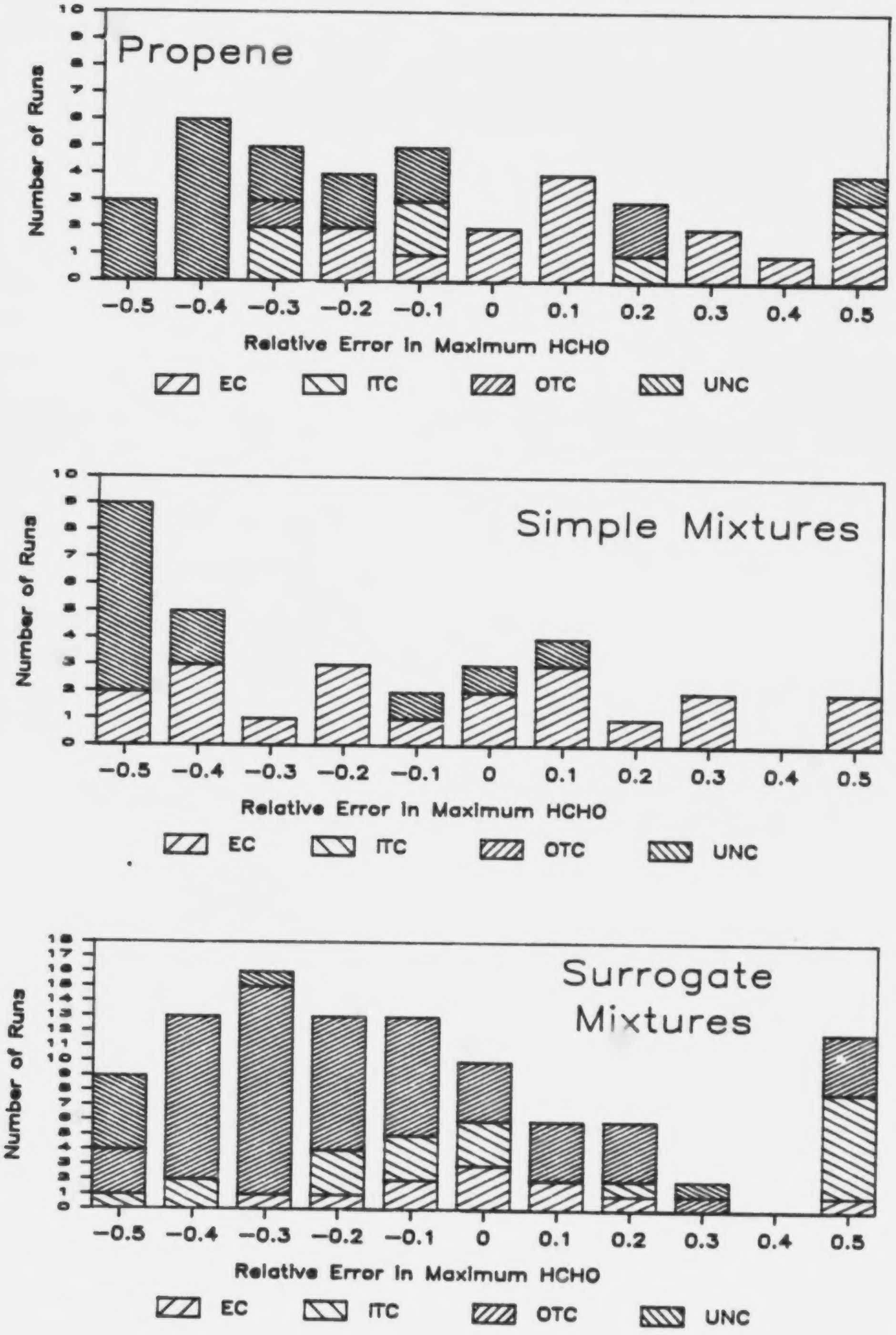


Figure 2-17. Distribution of relative errors in maximum formaldehyde concentrations for propene, simple mixture, and surrogate mixture runs.

uncertainty in the mechanism and the data as discussed in Carter et al. (1986).

3. CONDENSATION OF THE MECHANISM

Numerical integration of the chemistry is the most computationally demanding task in photochemical AQS models. The computer memory and time requirements of these models are a strong function of the number of chemical species in the mechanism and a weak function of the number of reactions in the mechanism. When the most accurate numerical integration routines [i.e., refinements of those developed by Gear (1971)] are used to solve the chemistry, the computer resource requirements depend on the square of the number of integrated species. Thus, it is clearly important to eliminate any unimportant species and reactions from the chemical mechanism and lump similar species wherever possible prior to using the mechanism in AQS models.

Single-cell photochemical AQS models like OZIPM (Hogo and Whitten 1986) can accommodate fairly large chemical mechanisms because the task of integrating the chemistry in one cell for one diurnal cycle is fairly small. However, typical applications of Eulerian models such as the Urban Airshed Model (Reynolds et al. 1973) employ 1,000 to 5,000 computational cells and use large amounts of computer resources for integrating the chemistry. Thus, it is quite important to condense the chemistry to the maximum justifiable extent for these multi-cell models. Because of the differences in the allowable size of mechanisms in the two types of models, two versions of the surrogate species mechanism were developed. The first mechanism, shown in Tables 3-1 and 3-2, is intended for use in OZIPM and other single-cell models. This mechanism is referred to as the OZIPM mechanism in this report. It was developed from the detailed mechanism, shown in Table 2-2, using minimal condensation approximations. The OZIPM mechanism has 131 reactions and 50 species. Twelve of these species can safely be computed using the steady-state approximation and one of the species, H_2O, can be treated as a constant. The second mechanism, shown in Tables 3-3 and 3-4, is intended for use in multi-cell AQS models. It is referred to as the condensed mechanism in this report. It has 95 reactions and 36 species. Nine of the species concentrations can safely be computed from the steady-state approximation and one of the species, H_2O, is a constant. It was developed from the OZIPM mechanism by incorporating significant condensation assumptions and

TABLE 3-1. SAPRC/ERT OZIPM CHEMICAL MECHANISM SPECIES LIST

SPECIES	ABREVIATION
1. NITRIC OXIDE	NO
2. NITROGEN DIOXIDE	NO2
3. OZONE	O3
4. NITROUS ACID	HONO
5. NITRIC ACID	HNO3
6. PERNITRIC ACID	HNO4
7. NITROGEN PENTOXIDE	N2O5
8. NITROGEN TRIOXIDE	NO3
9. HYDROPEROXY RADICAL	HO2
10. HYDROGEN PEROXIDE	H2O2
11. CARBON MONOXIDE	CO
12. FORMALDEHYDE	HCHO
13. ACETALDEHYDE	ALD2
14. PROPIONALDEHYDE	RCHO
15. PEROXYACETYLNITRATE	PAN
16. PEROXYPROPIONYL NITRATE	PPN
17. TOTAL RO2 RADICALS	RO2
18. TOTAL RCO3 RADICALS	RCO3
19. ORGANIC PEROXIDE	ROOH
20. ACETONE	ACET
21. METHYL ETHYL KETONE	MEK
22. GLYOXAL	GLYX
23. GLYOXAL PAN	GPAN
24. METHYL GLYOXAL	MGLY
25. C4-C5 ALKANES	ALK4
26. >C5 ALKANES	ALK7
27. ALKYL NITRATE	ALKN
28. ETHENE	ETHE
29. PROPENE	PRPE
30. TRANS-2-BUTENE	TBUT
31. TOLUENE	TOLU
32. M-XYLENE	XYLE
33. 1,3,5 TRI-M-BENZENE	TMBZ
34. DICARBONYLS	DIAL
35. O-CRESOL	CRES
36. PHENOLS	PHEN
37. NITROPHENOL	NPHE
STEADY STATE SPECIES	
38. OXYGEN - SINGLET D	O*SD
39. OXYGEN - ATOMIC	O
40. HYDROXYL RADICAL	OH
41. ACETALDEHYDE RCO3	MCO3
42. PROPIONALDEHYDE RCO3	PCO3
43. GLYOXAL RCO3	GCO3
44. GENERAL RO2 #1	RO2R
45. GENERAL RO2 #2	R2O2
46. ALKYL NITRATE RO2	RO2N
47. PHENOL RO2	RO2P
48. BENZALDEHYDE N-RO2	BZN2
49. PHENOXY RADICAL	BZO
50. WATER VAPOR	H2O

TABLE 3-2. SAPRC/ERT OZIPM CHEMICAL MECHANISM

	REACTION	MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
1.	NO2 + HV ---> NO + O	RADIATION DEPENDENT		
2.	O ---> O3	8.12E+05	4.87E+07	1.10E+04*EXP(1282/T)
3.	O + NO2 ---> NO	9.30E-12	1.37E+04	
4.	O + NO2 ---> NO3	2.23E-12	3.29E+03	1.11E-13*EXP(894/T)
5.	NO + O3 ---> NO2	1.81E-14	2.68E+01	1.80E-12*EXP(-1370/T)
6.	NO2 + O3 ---> NO3	3.23E-17	4.77E-02	1.20E-13*EXP(-2450/T)
7.	NO + NO3 ---> 2.NO2	1.86E-11	2.75E+04	8.00E-12*EXP(252/T)
8.	NO + NO ---> 2.NO2	1.02E-19	1.50E-04	1.72E-20*EXP(529/T)
9.	NO2 + NO3 ---> N2O5	1.15E-12	1.71E+03	4.62E-13*EXP(273/T)
10.	N2O5 ---> NO2 + NO3	3.47E-02	2.08E+00	1.33E+15*EXP(-11379/T)
11.	N2O5 + H2O ---> 2.HNO3	1.00E-21	1.48E-06	
12.	NO2 + NO3 ---> NO + NO2	4.04E-16	5.98E-01	2.50E-14*EXP(-1229/T)
13.	NO3 + HV ---> NO	RADIATION DEPENDENT		
14.	NO3 + HV ---> NO2 + O	RADIATION DEPENDENT		
15.	O3 + HV ---> O	RADIATION DEPENDENT		
16.	O3 + HV ---> O*SD	RADIATION DEPENDENT		
17.	O*SD + H2O ---> 2.OH	2.20E-10	3.25E+05	
18.	O*SD ---> O	7.20E+08	4.32E+10	
19.	NO + OH ---> HONO	6.60E-12	9.75E+03	4.03E-13*EXP(833/T)
20.	HONO + HV ---> NO + OH	RADIATION DEPENDENT		
21.	NO2 + H2O ---> HONO - NO2 + HNO3	4.00E-24	5.91E-09	
22.	NO2 + OH ---> HNO3	1.13E-11	1.68E+04	9.57E-13*EXP(737/T)
23.	HNO3 + OH ---> NO3	1.28E-13	1.89E+02	9.40E-15*EXP(778/T)
24.	CO + OH ---> HO2	2.18E-13	3.22E+02	
25.	O3 + OH ---> HO2	6.78E-14	1.00E+02	1.60E-12*EXP(-942/T)
26.	NO + HO2 ---> NO2 + OH	8.28E-12	1.22E+04	3.70E-12*EXP(240/T)
27.	NO2 + HO2 ---> HNO4	1.37E-12	2.02E+03	1.02E-13*EXP(773/T)
28.	HNO4 ---> NO2 + HO2	8.22E-02	4.93E+00	4.35E+13*EXP(-10103/T)
29.	HNO4 + OH ---> NO2	4.00E-12	5.91E+03	
30.	O3 + HO2 ---> OH	2.01E-15	2.96E+00	1.40E-14*EXP(-579/T)
31.	HO2 + HO2 ---> H2O2	3.02E-12	4.46E+03	2.27E-13*EXP(771/T)
32.	HO2 + HO2 + H2O ---> H2O2	6.97E-30	2.54E-01	3.26E-34*EXP(2971/T)
33.	NO3 + HO2 ---> HNO3	3.02E-12	4.46E+03	2.27E-13*EXP(771/T)
34.	NO3 + HO2 + H2O ---> HNO3	6.97E-30	2.54E-01	3.26E-34*EXP(2971/T)
35.	H2O2 + HV ---> 2.OH	RADIATION DEPENDENT		
36.	H2O2 + OH ---> HO2	1.66E-12	2.45E+03	3.10E-12*EXP(-187/T)
37.	RO2 + NO ---> NO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
38.	RCO3 + NO ---> NO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
39.	RCO3 + NO2 ---> NO2	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
40.	RO2 + HO2 ---> HO2	3.00E-12	4.43E+03	
41.	RCO3 + HO2 ---> HO2	3.00E-12	4.43E+03	
42.	ROOH + HV ---> HO2 + OH	RADIATION DEPENDENT		
43.	RO2 + RO2 --->	1.00E-15	1.48E+00	
44.	RO2 + RCO3 --->	3.00E-12	4.43E+03	
45.	RCO3 + RCO3 --->	2.50E-12	3.69E+03	
46.	HCHO + HV ---> 2.HO2 + CO	RADIATION DEPENDENT		
47.	HCHO + HV ---> CO	RADIATION DEPENDENT		

TABLE 3-2. SAPRC/ERT OZIPM CHEMICAL MECHANISM (CONTINUED)

	REACTION		MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
48.	HCHO + OH	---> HO2 + CO	9.00E-12	1.33E+04	
49.	HCHO + NO3	---> HNO3 + HO2 + CO	5.97E-16	8.82E-01	6.00E-13*EXP(-2060/T)
50.	HCHO + HO2	---> RO2R + RO2	1.00E-14	1.48E+01	
51.	ALD2 + OH	---> MCO3 + RCO3	1.60E-11	2.36E+04	6.90E-12*EXP(250/T)
52.	ALD2 + HV	---> CO + HCHO + HO2 + RO2R + RO2	RADIATION	DEPENDENT	
53.	ALD2 + NO3	---> HNO3 + MCO3 + RCO3	2.50E-15	3.69E+00	3.00E-13*EXP(-1427/T)
54.	MCO3 + NO	---> NO2 + HCHO + RO2R + RO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
55.	MCO3 + NO2	---> PAN	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
56.	MCO3 + HO2	---> ROOH + HCHO	3.00E-12	4.43E+03	
57.	MCO3 + RO2	---> .5HO2 + HCHO + RO2	3.00E-12	4.43E+03	
58.	MCO3 + RCO3	---> HO2 + HCHO + RCO3	2.50E-12	3.69E+03	
59.	PAN	---> MCO3 + NO2 + RCO3	3.68E-04	2.21E-02	2.00E+16*EXP(-13542/T)
60.	RCHO + OH	---> RCO3 + PCO3	1.98E-11	2.93E+04	8.50E-12*EXP(252/T)
61.	RCHO + HV	---> ALD2 + HO2 + CO + RO2R + RO2	RADIATION	DEPENDENT	
62.	RCHO + NO3	---> HNO3 + PCO3 + RCO3	2.46E-15	3.63E+00	3.00E-13*EXP(-1432/T)
63.	PCO3 + NO	---> NO2 + ALD2 + RO2R + RO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
64.	PCO3 + NO2	---> PPN	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
65.	PCO3 + HO2	---> ROOH + ALD2	3.00E-12	4.43E+03	
66.	PCO3 + RO2	---> .5HO2 + ALD2 + RO2	3.00E-12	4.43E+03	
67.	PCO3 + RCO3	---> HO2 + ALD2 + RCO3	2.50E-12	3.69E+03	
68.	PPN	---> PCO3 + NO2 + RCO3	3.68E-04	2.21E-02	2.00E+16*EXP(-13542/T)
69.	ACET + HV	---> MCO3 + HCHO + RCO3 + RO2R + RO2	RADIATION	DEPENDENT	
70.	ACET + OH	---> MGLY + RO2R + RO2	2.29E-13	3.39E+02	1.00E-11*EXP(-1125/T)
71.	MEK + HV	---> MCO3 + ALD2 + RCO3 + RO2R + RO2	RADIATION	DEPENDENT	
72.	MEK + OH	---> 1.5R2O2 + 1.5RO2 + .5MCO3 + .5ALD2 + .5HCHO	9.85E-13	1.46E+03	1.20E-11*EXP(-745/T)
		+ .5PCO3 + RCO3			
73.	GLYX + HV	---> .13HCHO +1.87CO	RADIATION	DEPENDENT	
74.	GLYX + OH	---> .63HO2 +1.26CO + .37GCO3 + .37RCO3	1.15E-11	1.70E+04	
75.	GLYX + NO3	---> HNO3 + .63HO2 +1.26CO + .37GCO3 + .37RCO3	6.01E-16	8.88E-01	6.00E-13*EXP(-2058/T)
76.	GCO3 + NO2	---> GPAN	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
77.	GCO3 + NO	---> NO2 + HO2 + CO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
78.	GPAN	---> NO2 + GCO3 + RCO3	3.68E-04	2.21E-02	2.00E+16*EXP(-13542/T)
79.	GCO3 + HO2	---> ROOH + CO	3.00E-12	4.43E+03	
80.	GCO3 + RO2	---> .5HO2 + CO + RO2	3.00E-12	4.43E+03	
81.	GCO3 + RCO3	---> HO2 + CO + RCO3	2.50E-12	3.69E+03	
82.	MGLY + HV	---> MCO3 + HO2 + CO + RCO3	RADIATION	DEPENDENT	
83.	MGLY + OH	---> MCO3 + CO + RCO3	1.70E-11	2.51E+04	
84.	MGLY + NO3	---> HNO3 + MCO3 + CO + RCO3	2.50E-15	3.69E+00	3.00E-13*EXP(-1427/T)
85.	ALK4 + OH	--->B01*HCHO +B02*ALD2 +B03*RCHO +B04*ACET +B05*MEK	3.22E-12	4.76E+03	1.05E-11*EXP(-353/T)
		+B06*RO2N +B07*RO2R +B08*R2O2 +B09*RO2	SEE NOTE 1		
86.	ALK7 + OH	--->B10*HCHO +B11*ALD2 +B12*RCHO +B13*ACET +B14*MEK	6.16E-12	9.11E+03	1.62E-11*EXP(-288/T)
		+B15*RO2N +B16*RO2R +B17*R2O2 +B18*RO2	SEE NOTE 1		
87.	ALKN + OH	---> NO2 + .15MEK +1.05RCHO + .48ALD2 + .16HCHO	2.03E-12	3.00E+03	2.19E-11*EXP(-709/T)
		+1.39R2O2 +1.39RO2			
88.	RO2N + NO	---> ALKN	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
89.	RO2N + HO2	---> ROOH + MEK	3.00E-12	4.43E+03	
90.	RO2N + RO2	---> RO2 + .5HO2 + MEK	1.00E-15	1.48E+00	

TABLE 3-2. SAPRC/ERT OZIPM CHEMICAL MECHANISM (CONTINUED)

	REACTION		MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
91.	RO2N + RCO3	---> RCO3 + .5HO2 + MEK	3.00E-12	4.43E+03	
92.	R2O2 + NO	---> NO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
93.	R2O2 + HO2	---> ROOH	3.00E-12	4.43E+03	
94.	R2O2 + RO2	---> RO2	1.00E-15	1.48E+00	
95.	R2O2 + RCO3	---> RCO3	3.00E-12	4.43E+03	
96.	RO2R + NO	---> NO2 + HO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
97.	RO2R + HO2	---> ROOH	3.00E-12	4.43E+03	
98.	RO2R + RO2	---> .5HO2 + RO2	1.00E-15	1.48E+00	
99.	RO2R + RCO3	---> .5HO2 + RCO3	3.00E-12	4.43E+03	
100.	ETHE + OH	---> RO2R + RO2 +1.56HCHO + .22ALD2	8.54E-12	1.26E+04	2.15E-12*EXP(411/T)
101.	ETHE + O3	---> HCHO + .12HO2 + .42CO	1.74E-18	2.57E-03	1.20E-14*EXP(-2634/T)
102.	ETHE + O	---> HCHO + HO2 + CO + RO2R + RO2	7.29E-13	1.08E+03	1.04E-11*EXP(-792/T)
103.	ETHE + NO3	---> NO2 + 2.HCHO + R2O2 + RO2	1.10E-16	1.62E-01	2.00E-12*EXP(-2923/T)
104.	PRPE + OH	---> RO2R + HCHO + ALD2 + RO2	2.63E-11	3.89E+04	4.85E-12*EXP(504/T)
105.	PRPE + O3	---> .65HCHO + .5ALD2 +.285CO + .06OH +.165HO2 +.135RO2R +.135RO2	1.13E-17	1.67E-02	1.32E-14*EXP(-2105/T)
106.	PRPE + O	---> .6ACET + .4HCHO + .2ALD2 + .2HO2 + .6RO2R + .4CO + .6RO2	3.98E-12	5.88E+03	1.18E-11*EXP(-324/T)
107.	PRPE + NO3	---> NO2 + HCHO + ALD2 + R2O2 + RO2	7.57E-15	1.12E+01	5.00E-12*EXP(-1935/T)
108.	TBUT + OH	---> RO2R + 2.ALD2 + RO2	6.37E-11	9.42E+04	1.01E-11*EXP(549/T)
109.	TBUT + O3	---> ALD2 + .15CO + .27RO2R + .12OH + .21HO2 + .27RO2 + .30HCHO	2.00E-16	2.96E-01	9.08E-15*EXP(-1137/T)
110.	TBUT + O	---> MEK + .4HO2	2.34E-11	3.45E+04	2.26E-11*EXP(10/T)
111.	TBUT + NO3	---> NO2 + 2.ALD2 + R2O2 + RO2	3.79E-13	5.61E+02	1.00E-11*EXP(-975/T)
112.	TOLU + OH	---> .16CRES + .16HO2 + .84RO2R + .4DIAL + .84RO2 +.144MGLY +.114GLYX	6.19E-12	9.14E+03	2.10E-12*EXP(322/T)
113.	XYLE + OH	---> .17CRES + .17HO2 + .83RO2R + .83RO2 + .65DIAL +.316MGLY +.095GLYX	2.45E-11	3.62E+04	1.66E-11*EXP(116/T)
114.	TMBZ + OH	---> .17CRES + .17HO2 + .83RO2R + .83RO2 + .49DIAL + .86MGLY	6.20E-11	9.16E+04	
115.	DIAL + OH	---> PCO3 + RCO3	3.00E-11	4.43E+04	
116.	DIAL + HV	---> HO2 + CO + MCO3 + RCO3	RADIATION	DEPENDENT	
117.	CRES + OH	---> .2MGLY + .15RO2P + .85RO2R + RO2	4.00E-11	5.91E+04	
118.	CRES + NO3	---> HNO3 + BZO	2.20E-11	3.25E+04	
119.	RO2P + NO	---> NPHE	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
120.	RO2P + HO2	---> ROOH	3.00E-12	4.43E+03	
121.	RO2P + RO2	---> .5HO2 + RO2	1.00E-15	1.48E+00	
122.	RO2P + RCO3	---> .5HO2 + RCO3	3.00E-12	4.43E+03	
123.	BZO + NO2	---> NPHE	1.50E-11	2.22E+04	
124.	BZO + HO2	---> PHEN	3.00E-12	4.43E+03	
125.	BZO	---> PHEN	1.00E-03	6.00E-02	
126.	PHEN + OH	---> .2GLYX + .15RO2P + .85RO2R + RO2	2.80E-11	4.14E+04	
127.	PHEN + NO3	---> HNO3 + BZO	3.80E-12	5.62E+03	
128.	NPHE + NO3	---> HNO3 + BZN2	3.80E-12	5.62E+03	
129.	BZN2 + NO2	--->	1.50E-11	2.22E+04	
130.	BZN2 + HO2	---> NPHE	3.00E-12	4.43E+03	
131.	BZN2	---> NPHE	1.00E-03	6.00E-02	

TABLE 3-2. SAPRC/ERT OZIPM CHEMICAL MECHANISM (CONTINUED)

Notes:

1. Alkane product coefficents are temperature dependent. They are determined by interpolation from the values at the following three temperatures.

Coeff.	270 K	300 K	330 K
B01	0.197	0.189	0.188
B02	0.168	0.315	0.582
B03	0.115	0.166	0.244
B04	0.351	0.339	0.350
B05	0.489	0.442	0.267
B06	0.114	0.073	0.050
B07	0.886	0.927	0.950
B08	0.446	0.599	0.807
B09	1.332	1.526	1.757
B10	0.005	0.023	0.054
B11	0.021	0.032	0.081
B12	0.215	0.249	0.296
B13	0.297	0.355	0.419
B14	0.765	0.882	0.891
B15	0.288	0.190	0.126
B16	0.701	0.810	0.873
B17	0.651	0.837	1.004
B18	1.352	1.647	1.877

TABLE 3-3. SAPRC/ERT CONDENSED CHEMICAL MECHANISM SPECIES LIST

SPECIES	ABREVIATION
1. NITRIC OXIDE	NO
2. NITROGEN DIOXIDE	NO2
3. OZONE	O3
4. NITROUS ACID	HONO
5. NITRIC ACID	HNO3
6. PERNITRIC ACID	HNO4
7. NITROGEN PENTOXIDE	N2O5
8. NITROGEN TRIOXIDE	NO3
9. HYDROPEROXY RADICAL	HO2
10. CARBON MONOXIDE	CO
11. FORMALDEHYDE	HCHO
12. ACETALDEHYDE	ALD2
13. METHYL ETHYL KETONE	MEK
14. METHYL GLYOXAL	MGLY
15. PEROXYACYLNITRATE	PAN
16. TOTAL RO2 RADICALS	RO2
17. CH3CO3 RADICAL	MCO3
18. ALKYL NITRATE	ALKN
19. >C3 ALKANES	ALKA
20. ETHENE	ETHE
21. >C2 ALKENES	ALKE
22. TOLUENE	TOLU
23. HIGHER AROMATICS	AROM
24. UNKNOWN DICARBONYLS	DIAL
25. O-CRESOL	CRES
26. NITROPHENOLS	NPHE
STEADY STATE SPECIES	
27. OXYGEN - SINGLET D	O*SD
28. ATOMIC OXYGEN	O
29. HYDROXYL RADICAL	OH
30. GENERAL RO2 #1	RO2R
31. GENERAL RO2 #2	R2O2
32. ALKYL NITRATE RO2	RO2N
33. PHENOL RO2	RO2P
34. BENZALDEHYDE N-RO2	BZN2
35. PHENOXY RADICAL	BZO
36. WATER VAPOR	H2O

TABLE 3-4. SAPRC/ERT CONDENSED CHEMICAL MECHANISM

	REACTION	MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
1.	NO2 + HV ---> NO + O	RADIATION	DEPENDENT	
2.	O ---> O3	7.75E+05	4.65E+07	1.05E+04*EXP(1282/T)
3.	O + NO2 ---> NO	9.30E-12	1.37E+04	
4.	O + NO2 ---> NO3	2.23E-12	3.29E+03	1.11E-13*EXP(894/T)
5.	NO + O3 ---> NO2	1.81E-14	2.68E+01	1.80E-12*EXP(-1370/T)
6.	NO2 + O3 ---> NO3	3.23E-17	4.77E-02	1.20E-13*EXP(-2450/T)
7.	NO + NO3 ---> 2.NO2	1.86E-11	2.75E+04	8.00E-12*EXP(252/T)
8.	NO + NO ---> 2.NO2	9.68E-20	1.43E-04	1.64E-20*EXP(529/T)
9.	NO2 + NO3 ---> N2O5	1.15E-12	1.71E+03	4.62E-13*EXP(273/T)
10.	N2O5 ---> NO2 + NO3	3.47E-02	2.08E+00	1.33E+15*EXP(-11379/T)
11.	N2O5 + H2O ---> 2.HNO3	1.00E-21	1.48E-06	
12.	NO2 + NO3 ---> NO + NO2	4.04E-16	5.98E-01	2.50E-14*EXP(-1229/T)
13.	NO3 + HV ---> NO	RADIATION	DEPENDENT	
14.	NO3 + HV ---> NO2 + O	RADIATION	DEPENDENT	
15.	O3 + HV ---> O	RADIATION	DEPENDENT	
16.	O3 + HV ---> O*SD	RADIATION	DEPENDENT	
17.	O*SD + H2O ---> 2.OH	2.20E-10	3.25E+05	
18.	O*SD ---> O	7.20E+08	4.32E+10	
19.	NO + OH ---> HONO	6.60E-12	9.75E+03	4.03E-13*EXP(833/T)
20.	HONO + HV ---> NO + OH	RADIATION	DEPENDENT	
21.	NO2 + H2O ---> HONO - NO2 + HNO3	4.00E-24	5.91E-09	
22.	NO2 + OH ---> HNO3	1.14E-11	1.68E+04	9.58E-13*EXP(737/T)
23.	HNO3 + OH ---> NO3	1.28E-13	1.89E+02	9.40E-15*EXP(778/T)
24.	CO + OH ---> HO2	2.18E-13	3.22E+02	
25.	O3 + OH ---> HO2	6.78E-14	1.00E+02	1.60E-12*EXP(-942/T)
26.	NO + HO2 ---> NO2 + OH	8.28E-12	1.22E+04	3.70E-12*EXP(240/T)
27.	NO2 + HO2 ---> HNO4	1.37E-12	2.02E+03	1.02E-13*EXP(773/T)
28.	HNO4 ---> NO2 + HO2	8.22E-02	4.93E+00	4.35E+13*EXP(-10103/T)
29.	HNO4 + OH ---> NO2	4.00E-12	5.91E+03	
30.	O3 + HO2 ---> OH	2.01E-15	2.96E+00	1.40E-14*EXP(-579/T)
31.	HO2 + HO2 --->	3.02E-12	4.46E+03	2.27E-13*EXP(771/T)
32.	HO2 + HO2 + H2O --->	6.97E-30	2.54E-01	3.26E-34*EXP(2971/T)
33.	NO3 + HO2 ---> HNO3	3.02E-12	4.46E+03	2.27E-13*EXP(771/T)
34.	NO3 + HO2 + H2O ---> HNO3	6.97E-30	2.54E-01	3.26E-34*EXP(2971/T)
35.	RO2 + NO ---> NO	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
36.	RO2 + HO2 ---> HO2	3.00E-12	4.43E+03	
37.	RO2 + RO2 --->	1.00E-15	1.48E+00	
38.	RO2 + MCO3 ---> MCO3	3.00E-12	4.43E+03	
39.	HCHO + HV ---> 2.HO2 + CO	RADIATION	DEPENDENT	
40.	HCHO + HV ---> CO	RADIATION	DEPENDENT	
41.	HCHO + OH ---> HO2 + CO	9.00E-12	1.33E+04	
42.	HCHO + NO3 ---> HNO3 + HO2 + CO	5.97E-16	8.82E-01	6.00E-13*EXP(-2060/T)
43.	HCHO + HO2 ---> RO2R + RO2	1.00E-14	1.48E+01	
44.	ALD2 + OH ---> MCO3	1.60E-11	2.36E+04	6.90E-12*EXP(250/T)
45.	ALD2 + HV ---> CO + HCHO + HO2 + RO2R + RO2	RADIATION	DEPENDENT	
46.	ALD2 + NO3 ---> HNO3 + MCO3	2.50E-15	3.69E+00	3.00E-13*EXP(-1427/T)
47.	MCO3 + NO ---> NO2 + HCHO + RO2R + RO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
48.	MCO3 + NO2 ---> PAN	5.12E-12	7.57E+03	2.80E-12*EXP(180/T)
49.	MCO3 + HO2 ---> HCHO	3.00E-12	4.43E+03	
50.	MCO3 + MCO3 ---> 2.HO2 + 2.HCHO	2.50E-12	3.69E+03	
51.	PAN ---> MCO3 + NO2	3.68E-04	2.21E-02	2.00E+16*EXP(-13542/T)

TABLE 3-4. SAPRC/ERT CONDENSED CHEMICAL MECHANISM (CONTINUED)

	REACTION		MOLECULE-CC-SEC (298 K)	PPM-MIN (298 K)	EXPRESSION
52.	MEK + HV	---> ALD2 + MCO3 + RO2R + RO2	RADIATION	DEPENDENT	
53.	MEK + OH	---> 1.5RO2R + 1.5RO2 + MCO3 + .5ALD2 + .5HCHO	9.85E-13	1.46E+03	1.20E-11*EXP(-745/T)
54.	MGLY + HV	---> MCO3 + HO2 + CO	RADIATION	DEPENDENT	
55.	MGLY + OH	---> MCO3 + CO	1.70E-11	2.51E+04	
56.	MGLY + NO3	---> HNO3 + MCO3 + CO	2.50E-15	3.69E+00	3.00E-13*EXP(-1427/T)
57.	ALKA + OH	--->B01*HCHO +B02*ALD2 +B03*MEK +B04*RO2N +B05*RO2R +B06*R2O2 +B07*RO2	SEE NOTE 1		
58.	ALKN + OH	---> NO2 + .15MEK +1.53ALD2 + .16HCHO +1.39R2O2 +1.39RO2	2.03E-12	3.00E+03	2.19E-11*EXP(-709/T)
59.	RO2N + NO	---> ALKN	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
60.	RO2N + HO2	---> MEK	3.00E-12	4.43E+03	
61.	RO2N + RO2	---> RO2 + .5HO2 + MEK	1.00E-15	1.48E+00	
62.	RO2N + MCO3	---> HCHO + HO2 + MEK	3.00E-12	4.43E+03	
63.	R2O2 + NO	---> NO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
64.	R2O2 + HO2	--->	3.00E-12	4.43E+03	
65.	R2O2 + RO2	---> RO2	1.00E-15	1.48E+00	
66.	R2O2 MCO3	---> HCHO + HO2	3.00E-12	4.43E+03	
67.	RO2R + NO	---> NO2 + HO2	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
68.	RO2R + HO2	--->	3.00E-12	4.43E+03	
69.	RO2R + RO2	---> .5HO2 + RO2	1.00E-15	1.48E+00	
70.	RO2R + MCO3	---> HCHO + HO2	3.00E-12	4.43E+03	
71.	ETHE + OH	---> RO2R + RO2 +1.56HCHO + .22ALD2	8.54E-12	1.26E+04	2.15E-12*EXP(411/T)
72.	ETHE + O3	---> HCHO + .12HO2 + .42CO	1.74E-18	2.57E-03	1.20E-14*EXP(-2634/T)
73.	ETHE + O	---> HCHO + HO2 + CO + RO2R + RO2	7.29E-13	1.08E+03	1.04E-11*EXP(-792/T)
74.	ETHE + NO3	---> NO2 + 2.HCHO + R2O2 + RO2	1.09E-16	1.61E-01	2.00E-12*EXP(-2925/T)
75.	ALKE + OH	--->B08*HCHO +B09*ALD2 + RO2R + RO2	SEE NOTE 1		
76.	ALKE + O3	--->B10*HCHO +B11*ALD2 +B12*RO2R +B12*RO2 +B13*HO2 +B14*OH +B15*CO	SEE NOTE 1		
77.	ALKE + O	--->B16*CO +B17*MEK +B18*HCHO +B19*ALD2 +B20*HO2 +B21*RO2R +B21*RO2	SEE NOTE 1		
78.	ALKE + NO3	---> NO2 +B08*HCHO +B09*ALD2 + R2O2 + RO2	SEE NOTE 1		
79.	TOLU + OH	---> .16CRES + .16HO2 + .84RO2R + .4DIAL + .84RO2 +.144MGLY +.114HCHO +.114CO	6.19E-12	9.14E+03	2.10E-12*EXP(322/T)
80.	AROM + OH	---> .17CRES + .17HO2 + .83RO2R + .83RO2 +B22*DIAL +B23*MGLY +B24*HCHO +B24*CO	SEE NOTE 1		
81.	DIAL + OH	---> MCO3	3.00E-11	4.43E+04	
82.	DIAL + HV	---> HO2 + CO + MCO3	RADIATION	DEPENDENT	
83.	CRES + OH	---> .2MGLY + .15RO2P + .85RO2R + RO2	4.00E-11	5.91E+04	
84.	CRES + NO3	---> HNO3 + BZO	2.20E-11	3.25E+04	
85.	RO2P + NO	---> NPHE	7.68E-12	1.14E+04	4.20E-12*EXP(180/T)
86.	RO2P + HO2	--->	3.00E-12	4.43E+03	
87.	RO2P + RO2	---> .5HO2 + RO2	1.00E-15	1.48E+00	
88.	RO2P + MCO3	---> HCHO + HO2	3.00E-12	4.43E+03	
89.	BZO + NO2	---> NPHE	1.50E-11	2.22E+04	
90.	BZO + HO2	--->	3.00E-12	4.43E+03	
91.	BZO	--->	1.00E-03	6.00E-02	
92.	NPHE + NO3	---> HNO3 + BZN2	3.80E-12	5.62E+03	
93.	BZN2 + NO2	--->	1.50E-11	2.22E+04	
94.	BZN2 + HO2	---> NPHE	3.00E-12	4.43E+03	
95.	BZN2	---> NPHE	1.00E-03	6.00E-02	

TABLE 3-4. SAPRC/ERT CONDENSED CHEMICAL MECHANISM (CONTINUED)

NOTES:

1. The variable product coefficents (Bi) and lumped rate constants (Rj) are defined below. The alkane product coefficients are given at three temperatures. Values of the coefficients at intermediate temperatures can be obtained by linear interpolation. Rate constants are given in molecule-cc-sec units. The following fractions must be specified to determine the varaible coefficients.

A = C4-C5 fraction of >C3 alkanes on a carbon basis
B = Terminal alkene fraction of >C2 alkenes on a carbon basis
C = Di-alkylbenzene fraction of di- & tri-alkylbenzenes on a carbon basis.

X = C4-C5 fraction of >C3 alkanes on a mole basis
Y = Terminal alkene fraction of >C2 alkenes on a mole basis
Z = Di-alkylbenzene fraction of di- & tri-alkylbenzenes on a mole basis.
X = (A/4.5) / (A/4.5 + (1.-A)/7.)
Y = (B/3.0) / (B/3.0 + (1.-B)/4.)

Z = (C/8.0) / (C/8.0 + (1.-C)/9.)

Coeff.	at 270 K	at 300 K	at 330 K
B01 =	0.197*X + 0.005*(1-X)	0.189*X + 0.023*(1-X)	0.188*X + 0.054*(1-X)
B02 =	0.282*X + 0.236*(1-X)	0.481*X + 0.281*(1-X)	0.826*X + 0.377*(1-X)
B03 =	0.489*X + 0.765*(1-X)	0.442*X + 0.882*(1-X)	0.267*X + 0.891*(1-X)
B04 =	0.114*X + 0.288*(1-X)	0.073*X + 0.190*(1-X)	0.050*X + 0.126*(1-X)
B05 =	0.886*X + 0.701*(1-X)	0.927*X + 0.810*(1-X)	0.950*X + 0.873*(1-X)
B06 =	0.446*X + 0.651*(1-X)	0.599*X + 0.837*(1-X)	0.807*X + 1.004*(1-X)
B07 =	1.332*X + 1.352*(1-X)	1.526*X + 1.647*(1-X)	1.757*X + 1.877*(1-X)

B08 = Y
B09 = Y + 2.00*(1-Y)
B10 = 0.64*Y
B11 = 0.50*Y + (1-Y)
B12 = 0.13*Y + 0.27*(1-Y)
B13 = 0.17*Y + 0.21*(1-Y)
B14 = 0.06*Y + 0.12*(1-Y)
B15 = 0.28*Y
B16 = 0.40*Y
B17 = (1-Y)
B18 = 0.40*Y
B19 = 0.20*Y
B20 = 0.20*Y + 0.40*(1-Y)
B21 = 0.60*Y

B22 = 0.650*Z + 0.49*(1-Z)
B23 = 0.316*Z + 0.86*(1-Z)
B24 = 0.095*Z

R57 = 1.053E-11*EXP(-354/T)*X + 1.62E-11*EXP(-289/T)*(1-X)
R75 = 4.850E-12*EXP(504/T)*Y + 1.01E-11*EXP(549/T)*(1-Y)
R76 = 1.320E-14*EXP(-2105/T)*Y + 9.08E-15*EXP(-1137/T)*(1-Y)
R77 = 1.180E-11*EXP(-324/T)*Y + 2.26E-11*EXP(10/T)*(1-Y)
R78 = 5.000E-12*EXP(-1935/T)*Y + 1.00E-11*EXP(-975/T)*(1-Y)
R80 = 1.660E-11*EXP(116/T)*Z + 6.20E-11*(1-Z)

approximations. The major distinction between the mechanisms is the number of organic precursor species and oxygenated species in the mechanisms. Table 3-5 summaries the organic precursor and oxygenated species in each of the mechanisms.

The philosophy used in this research program was to develop and test detailed explicit chemical mechanisms against the smog chamber data base and, subsequently, condense the mechanism for use in AQS models. The validity of condensed mechanisms was determined by testing against the detailed mechanism for a range of conditions characteristic of the ambient atmosphere. In urban-scale atmospheric modeling, the mechanisms are always applied to complex mixtures of organics. Minor pathways included in the explicit reaction mechanisms can often be ignored or lumped without significantly affecting the mechanism performance on complex mixture simulations. Thus, while some testing of the condensed against the detailed mechanism was performed for single organics, most of the testing was performed for simple and complex mixtures of organics in typical urban air. Generally, only condensation assumptions that had little or no effect on the predictions were incorporated into the OZIPM mechanism. Larger discrepancies between the condensed and OZIPM mechanisms were tolerated because of the need to minimize the number of species in multi-cell models. Nevertheless, these discrepancies were small, which reflects the generally conservative philosophy used in this condensation effort.

Mechanism condensation is not a mysterious process. It generally proceeds in a stepwise fashion from the condensation steps that have trivial effects to those that have substantial effects. Each of the condensation assumptions or steps incorporated into the AQS model mechanisms is described in this section. Almost every approximation was investigated independently as well as in conjunction with the other approximations. Thus, these mechanisms have been synthesized from a large amount of testing.

3.1 The OZIPM Mechanism

The inorganic chemistry was not materially changed for either of the AQS model mechanisms. The important inorganic species and reactions were

TABLE 3-5

SURROGATE SPECIES IN THE MECHANISMS

DETAILED MECHANISM	OZIPM MECHANISM	CONDENSED MECHANISM
PROPANE		
C4-C5 ALKANES	C4-C5 ALKANES	>C3 ALKANES
>C5 ALKANES	>C5 ALKANES	
ETHENE	ETHENE	ETHENE
PROPENE	PROPENE	
1-BUTENE		HIGHER ALKENES
TRANS-2-BUTENE	TRANS-2-BUTENE	
ISO-BUTENE		
BENZENE		
TOLUENE	TOLUENE	TOLUENE
M-XYLENE	M-XYLENE	HIGHER AROMATICS
MESITYLENE	MESITYLENE	
FORMALDEHYDE	FORMALDEHYDE	FORMALDEHYDE
ACETALDEHYDE	ACETALDEHYDE	ACETALDEHYDE
GLYCOL ALDEHYDE		
PROPIONALDEHYDE	PROPIONALDEHYDE	
BENZALDEHYDE		
ACETONE	ACETONE	
METHYL ETHYL KETONE	METHYL ETHYL KETONE	METHYL ETHYL KETONE
GLYOXAL	GLYOXAL	
METHYL GLYOXAL	METHYL GLYOXAL	METHYL GLYOXAL
UNKNOWN AROMATIC RING-OPENING PROD 1	UNKNOWN AROMATIC RING-OPENING PROD.	UNKNOWN AROMATIC RING-OPENING PROD.
UNKNOWN AROMATIC RING-OPENING PROD. 2		

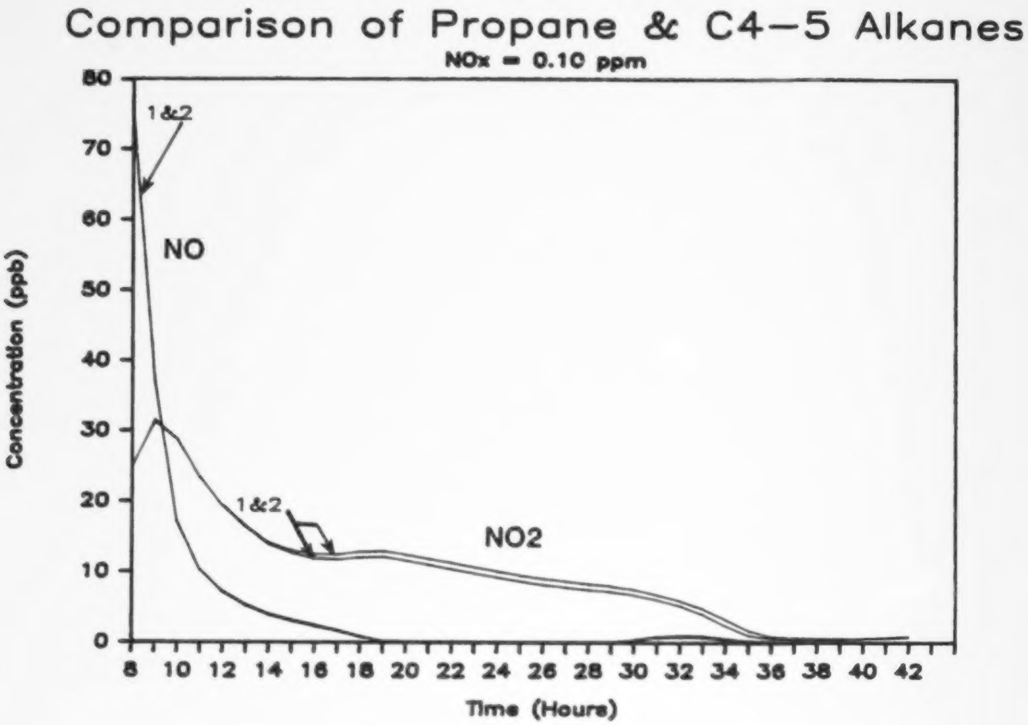
carefully selected at the time the detailed mechanism was formulated. None of the reactions can safely be eliminated for urban applications. However, the concentrations of species with relatively constant concentrations, such as M, O_2, and H_2O, can be incorporated into the reaction rate constants. These species are important reactants in the mechanism; however, they are so abundant in the lower atmosphere that these reactions do not significantly influence their concentrations. M and O_2 were included as species in the detailed mechanism mostly for the sake of chemical fidelity and clarity. They were eliminated from the OZIPM mechanism by incorporating values appropriate for the lower atmosphere (i.e., [M] = 2.49E19 and $[O_2]$ = 5.22E18 molecules/cc at 1 atm and 298°K) into the appropriate rate constants (reactions 2, 4, 18, 32, and 36 in Table 2-2). Similarly, the user may chose to incorporate the water vapor concentration into the rate constants (for reactions 11, 17, 21, 33, 34, 37 and 38 in Table 2-2). The recommended default concentration of H_2O is 5.E17 molecule/cc or 2.E4 ppm.

The form of the rate constant expressions for numerous inorganic reactions is too complex to be input to standard kinetic solver packages such as OZIPM. These rate expressions can be well approximated over the typical photochemical oxidant season temperature range using the standard rate expression instead of the complex expression reported in the literature and used in the detailed mechanism. As part of the adaptation and condensation, these expressions were fitted to the standard rate expression, $k = A \exp(-E/RT)$, over the 270 to 330°K temperature range. The rate constant expressions affected were those for reactions 2, 4, 9, 10, 19, 22, 27, and 28 in Table 2-2.

The inorganic reactions involving $HO_2 + HO_2$ and $HO_2 + NO_3$ were represented using fewer reactions in the OZIPM mechanism. When M and O_2 are treated as constants, reactions 31-32, 33-34, 35-36, and 37-38 in Table 2-2 can be represented as reactions 31, 32, 33, and 34 in Table 3-2, respectively, without any loss of accuracy.

Dinitrophenols (DNPH) were eliminated from the species list in the OZIPM mechanism. This species is only a product in the mechanism (see reaction 158 in Table 2-2), so its elimination has no effect on the predictions for other species. Its concentration is integrated in the detailed mechanism because it is a significant nitrogen sink in the aromatic mechanism.

As discussed in Section 2, the detailed mechanism includes reactions for the oxidation of propane and benzene. These two compounds are among the most abundant of the less reactive NMOC found in urban air. It is not uncommon for each of these compounds to account for 2-3% of the NMOC. This is in fact why propane and benzene were selected as surrogate species for less reactive compounds. The contributions of these species to ozone formation in urban areas is believed to be quite small under most circumstances. The reactions for propane and benzene were eliminated from the OZIPM mechanism because they contribute so little reactivity in most simulations and because their reactivity can adequately be represented by partial assignment of their emissions (or initial concentrations) to the C4-C5 alkanes class. Figures 3-1 and 3-2 compare predictions of NO, NO_2, and ozone in simulations with propane represented explicitly and as 50% C4-C5 alkanes and 50% nonreactive (on a carbon basis). These figures show results for simulations of 1.5 ppmC propane with 0.1 and 0.05 ppm NO_x (NMOC/NO_x ratios of 15 and 30). Other inputs for the simulation are summarized in Table 3-6. The results clearly indicate that this approximate treatment of propane emissions provides excellent simulation of the NO_x oxidation rate and ozone formation at two different NMOC/NO_x ratios. Figures 3-3 and 3-4 show the NO, NO_2, and O3 predictions for comparable simulations of benzene/NO_x systems. The figures show comparisons of the results using the benzene mechanism to the results with benzene represented as 30% C4-C5 alkanes and 70% nonreactive. The figures show good agreement for the NO_x oxidation rate and for the ozone formation rates on the first day of the simulations. On the second day of the simulation with the lower NMOC/NO_x ratio, the approximation of benzene as 30% C4-C5 alkanes results in 15% overprediction of the ozone yield. Since this discrepancy is small and only occurs on the second day, this approximation is considered acceptable. Thus, we recommend treating propane and benzene as 50% and 30% C4-C5 alkanes, respectively, in urban ozone modeling. Elimination of the reactions for propane and benzene eliminates three species from the mechanism (ALK3, BENZ, BGLY).



1: 1.5 ppmC Propane
2: 0.75ppmC C4–C5 Alkanes

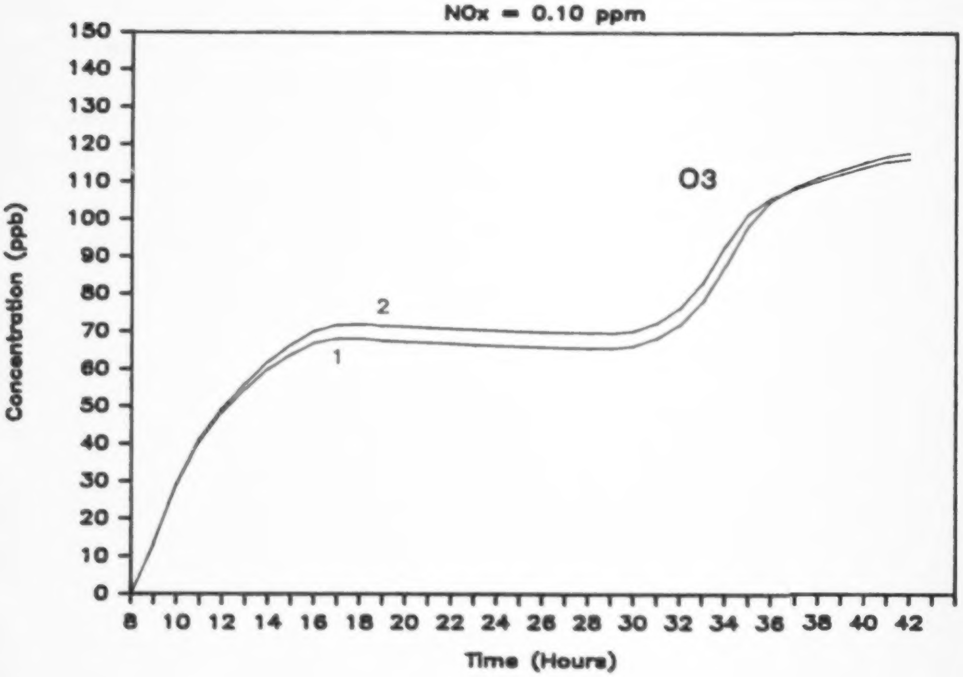


Figure 3-1. Comparison of NO, NO_2, and O_3 predictions for mixtures with 1.5 ppmC propane + 0.10 ppm NO_x and 0.75 ppmC C4-C5 alkanes + 0.10 ppm NO_x.

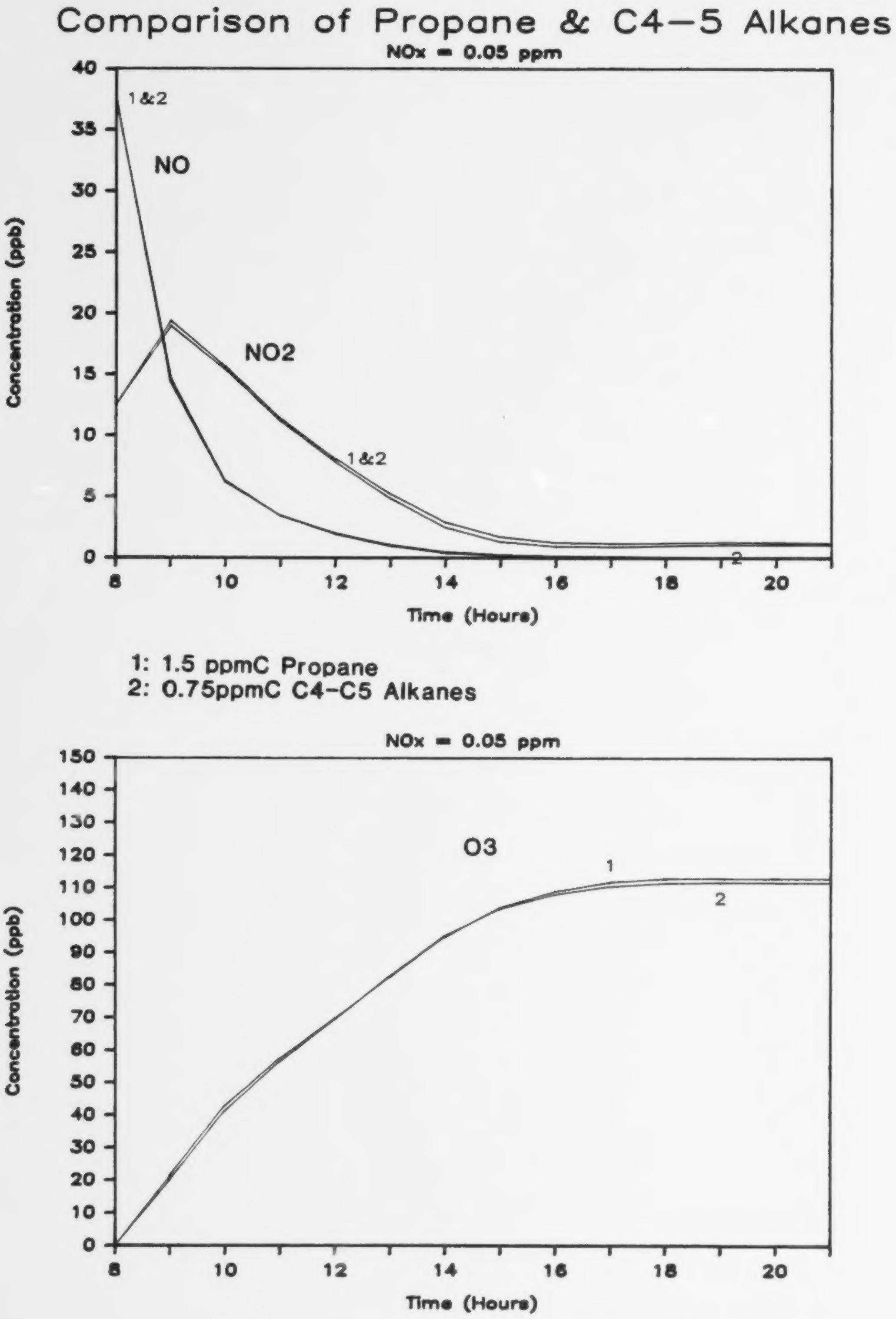


Figure 3-2. Comparison of NO, NO_2, and O_3 predictions for mixtures with 1.5 ppmC propane + 0.05 ppm NO_x and 0.75 ppmC C4-C5 alkanes + 0.05 ppm NO_x.

Table 3-6

Conditions for Mechanism Comparison Simulations

Solar Radiation Inputs:

Place:	Los Angeles, CA
Lattitude:	34.
Longitude:	118.
Time Zone:	8.
Date:	June 21, 1986
Photolysis Rates:	Table 2-4
Mixing Heights:	250 m at 0600 Hours 250 m at 0800 " 390 m at 0900 " 565 m at 1000 " 729 m at 1100 " 850 m at 1200 " 937 m at 1300 " 1000 m at 1400 " 1000 m at 2000 "
Temperature:	30 C
Ozone aloft:	0.08 ppm
Initial Values:	[CO] = 1 ppm [O3] = 0.01 ppb [H2O] = 20,000 ppm [HCHO] = 10 ppb in alkane and benzene runs only
NO/NOx Ratio:	0.75
NMOC/NOx:	3, 5, 10, 15, 20, 30 ppmC/ppm
Post 6 AM Emissions:	None

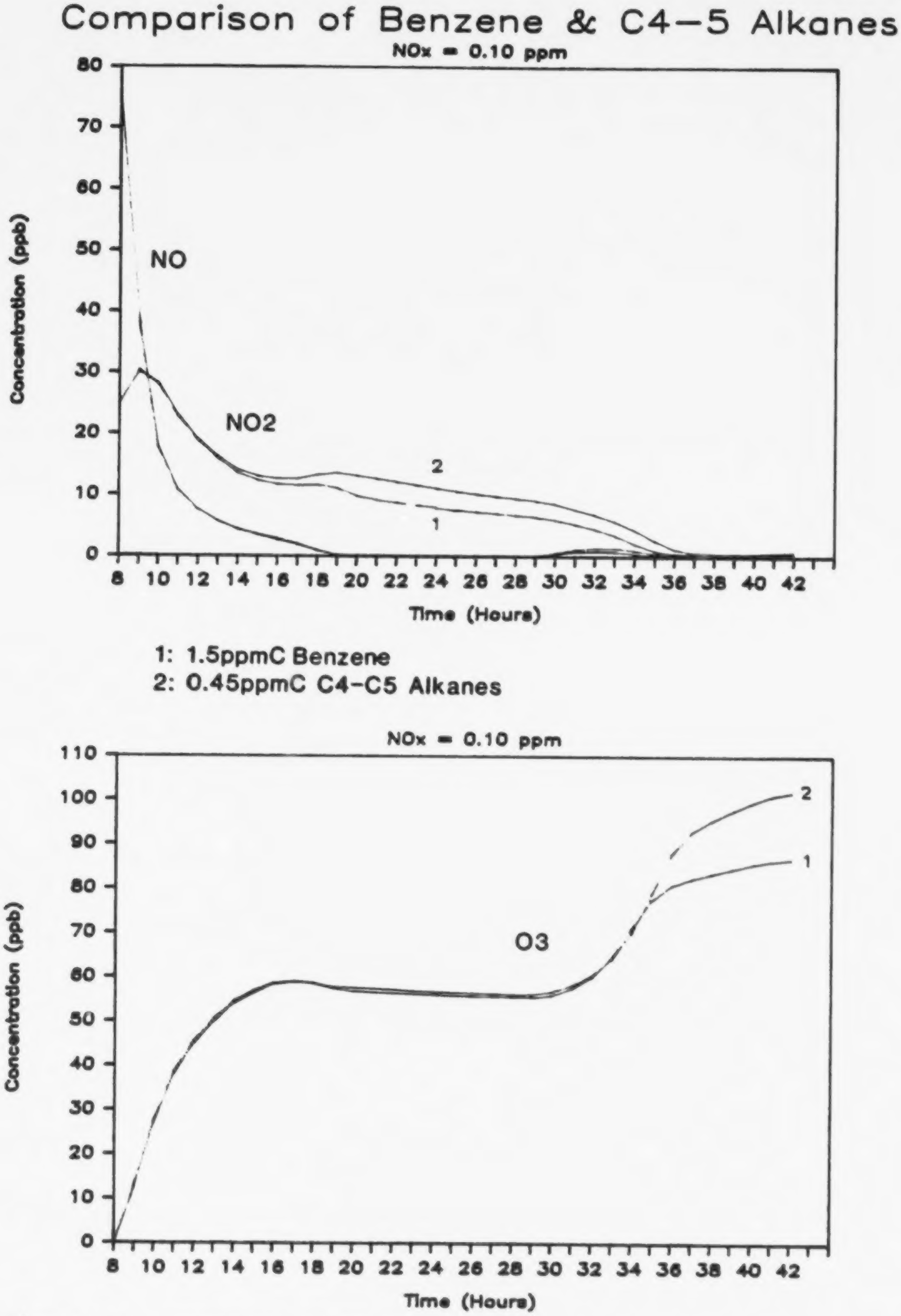


Figure 3-3. Comparison of NO, NO_2, and O_3 predictions for mixtures with 1.5 ppmC benzene + 0.10 ppm NO_x and 0.45 ppmC C4-C5 alkanes + 0.10 ppm NO_x.

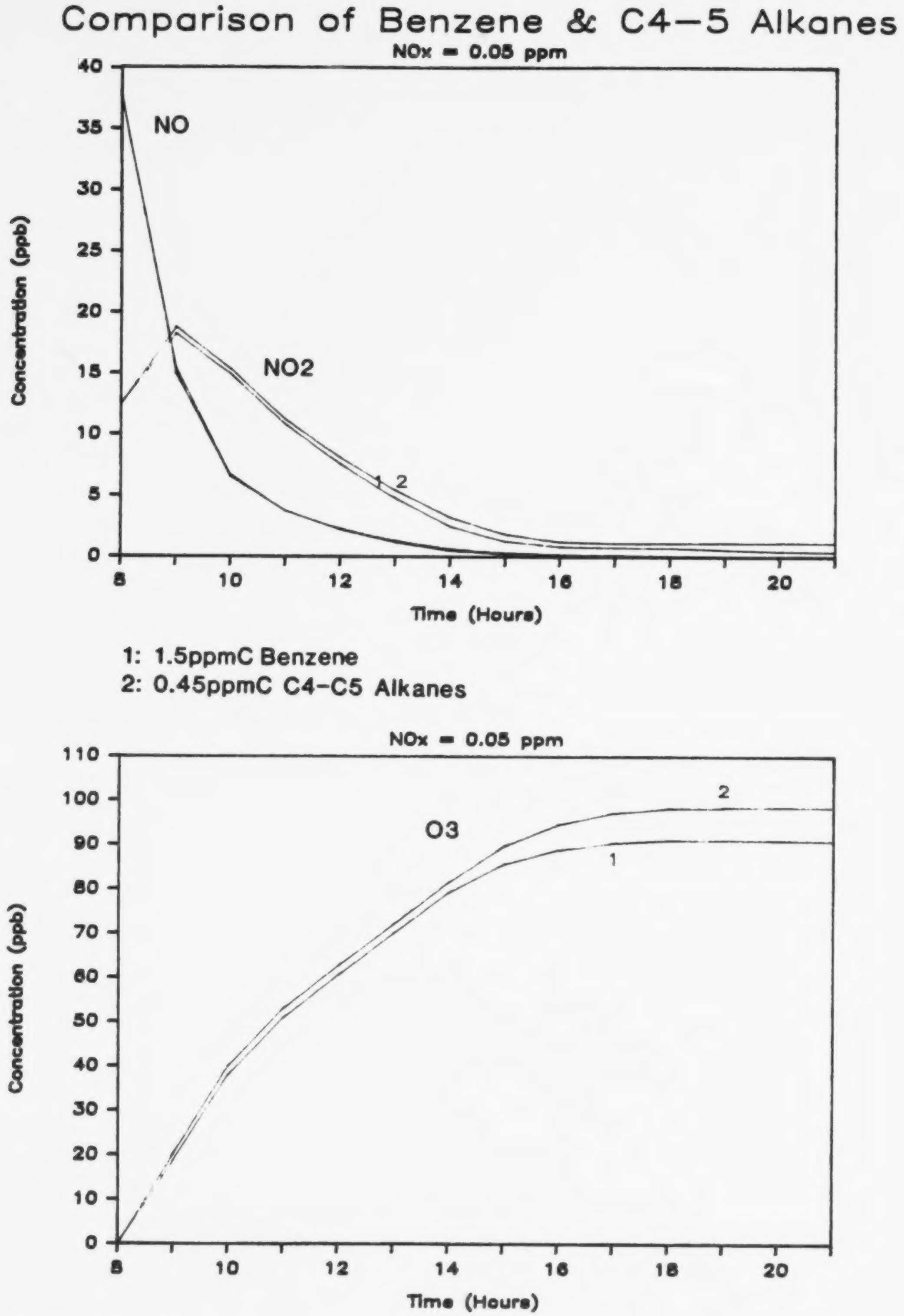


Figure 3-4. Comparison of NO, NO_2, and O_3 predictions for mixtures with 1.5 ppmC benzene + 0.05 ppm NO_x and 0.45 ppmC C4-C5 alkanes + 0.05 ppm NO_x.

The ethene chemistry incorporated into the detailed mechanism has glycolaldehyde (GCHO) as a minor product of ethene's reaction with OH. This is the only source of glycolaldehyde in the mechanism. The chemistry of glycolaldehyde is very similar to the chemistry of acetaldehyde. Tests were made to determine if the glycolaldehyde chemistry could be represented by the acetaldehyde chemistry. Figures 3-5 and 3-6 show the results of simulations with 1 ppmC ethene and 0.33 and 0.20 ppm NO_x, respectively, with acetaldehyde substituted for glycolaldehyde in the OZIPM mechanism. Other conditions for this simulation are described in Table 3-6. The results show that NO and NO_2 are essentially unaffected by the substitution. The results for ozone also show excellent agreement. The ozone predicted with the OZIPM mechanism is within 2% of the concentrations predicted with the mechanism. The good agreement obtained in these tests on pure ethene-NO_x systems provides ample justification for treating glycolaldehyde as acetaldehyde and, thereby, eliminating three more species from the mechanism (GCHO, GAO3, PANG).

Another minor product in the detailed aromatic mechanism is benzaldehyde (BCHO). The benzaldehyde yields from toluene, m-xylene, and mesitylene are 0.08, 0.04, and 0.02, respectively. Benzaldehyde is not very reactive under ideal circumstances and is generally recognized as contributing negative reactivity to NMOC mixtures (Atkinson et al. 1983). Tests were made to examine the effects of ignoring the benzaldehyde reactions in the mechanism for OZIPM. Figures 3-7 and 3-8 compare the predictions of toluene-NO_x simulations at NMOC/NO_x ratios of 5 and 10, respectively, with and without the benzaldehyde reactions. Figures 3-9 and 3-10 show similar results for m-xylene-NO_x systems with and without benzaldehyde reactions at the same two NMOC/NO_x ratios. The results indicate benzaldehyde has negligible effects on the NO and NO_2 concentration profiles. For ozone, the level of agreement is also quite good (within 2%). Ignoring the benzaldehyde reactions results in slightly more ozone in the simulations (see the lower NMOC/NO_x ratio cases), which confirms its negative reactivity contribution. Given that its contribution is so small in pure aromatic-NO_x systems, the benzaldehyde chemistry can safely be ignored in urban ozone modeling. This step eliminates three species from the mechanism (BCHO, BAO3, and PBZN).

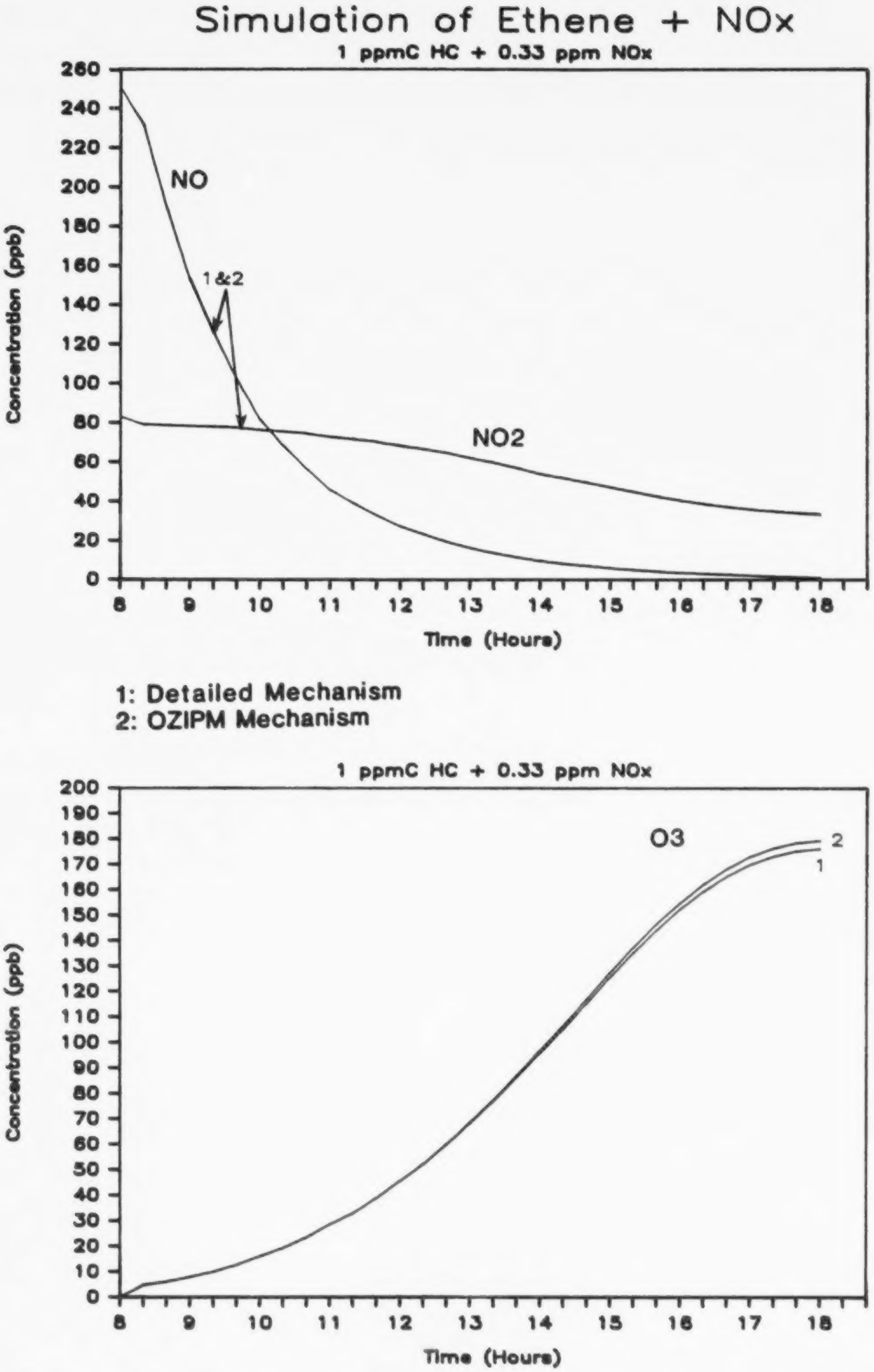


Figure 3-5. Comparison of NO, NO_2, and O_3 predictions for 1 ppmC ethene + 0.33 ppm NO_x with the detailed and OZIPM mechanisms.

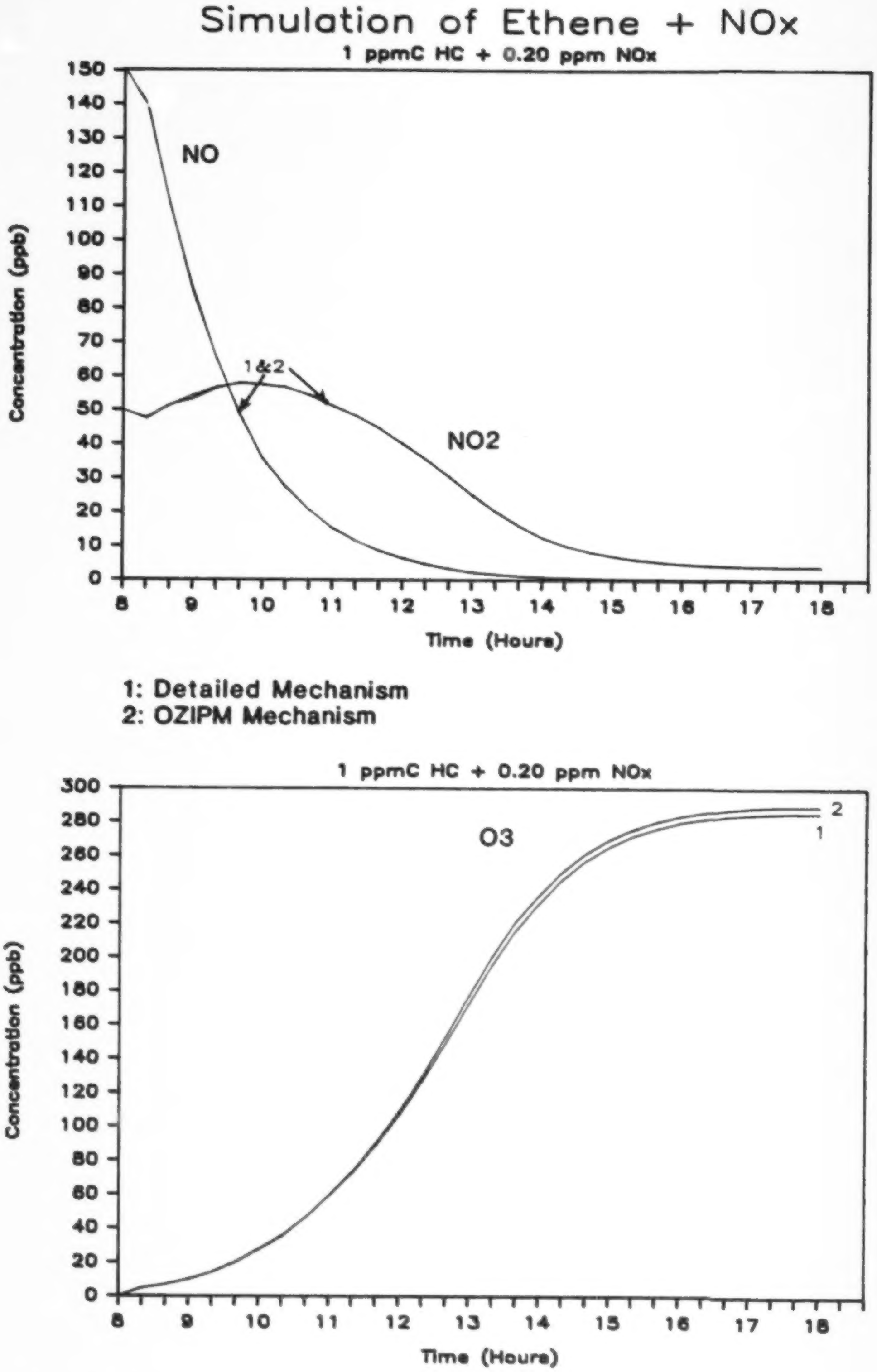


Figure 3-6. Comparison of NO, NO_2, and O_3 predictions for 1 ppmC ethene + 0.20 ppm NO_x with the detailed and OZIPM mechanisms.

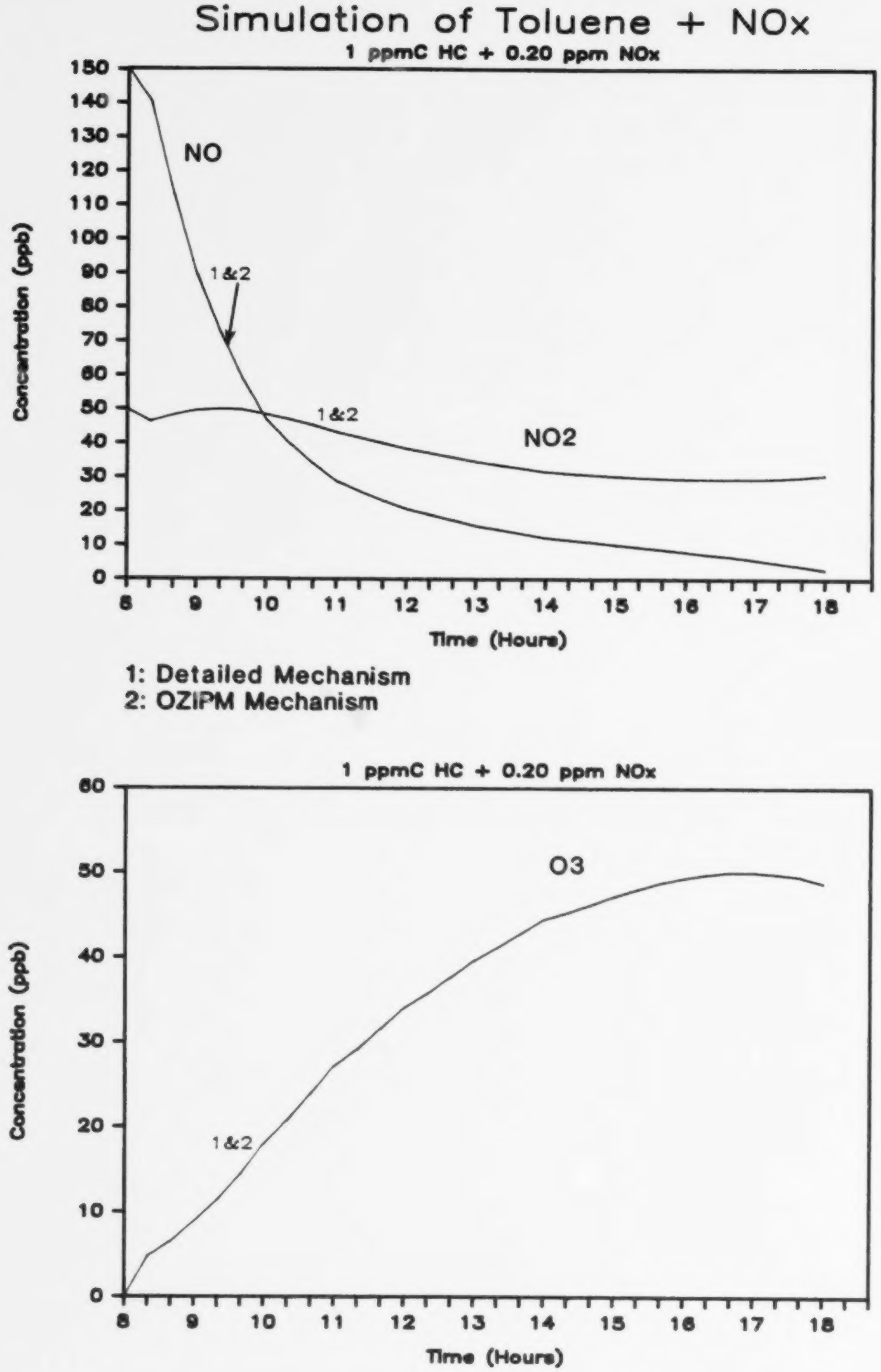


Figure 3-7. Comparison of NO, NO_2, and O_3 predictions for 1 ppmC toluene + 0.20 ppm NO_x with detailed and OZIPM mechanism.

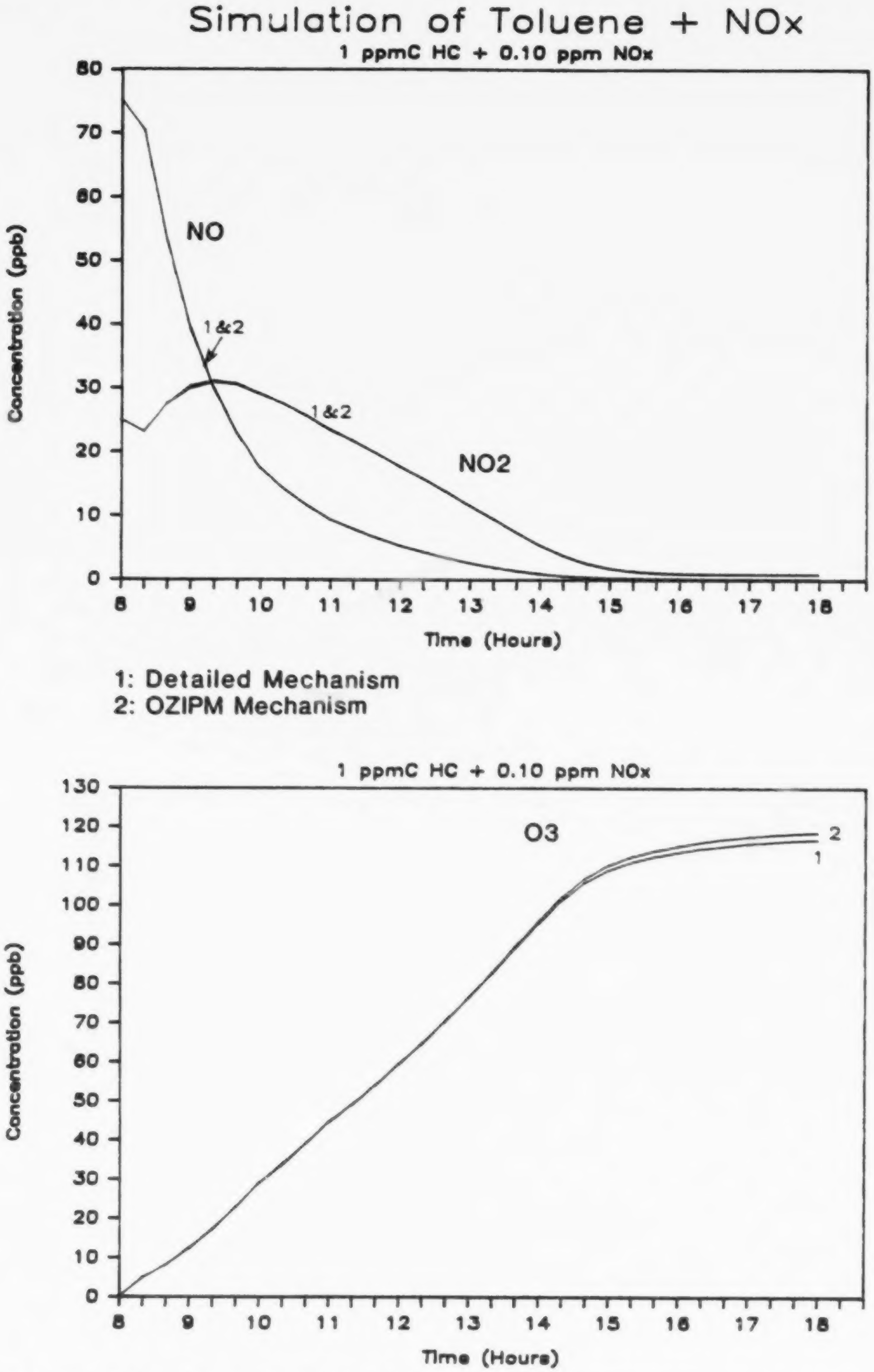


Figure 3-8. Comparison of NO, NO_2, and O_3 predictions for 1 ppmC toluene + 0.10 ppm NO_x with detailed and OZIPM mechanism.

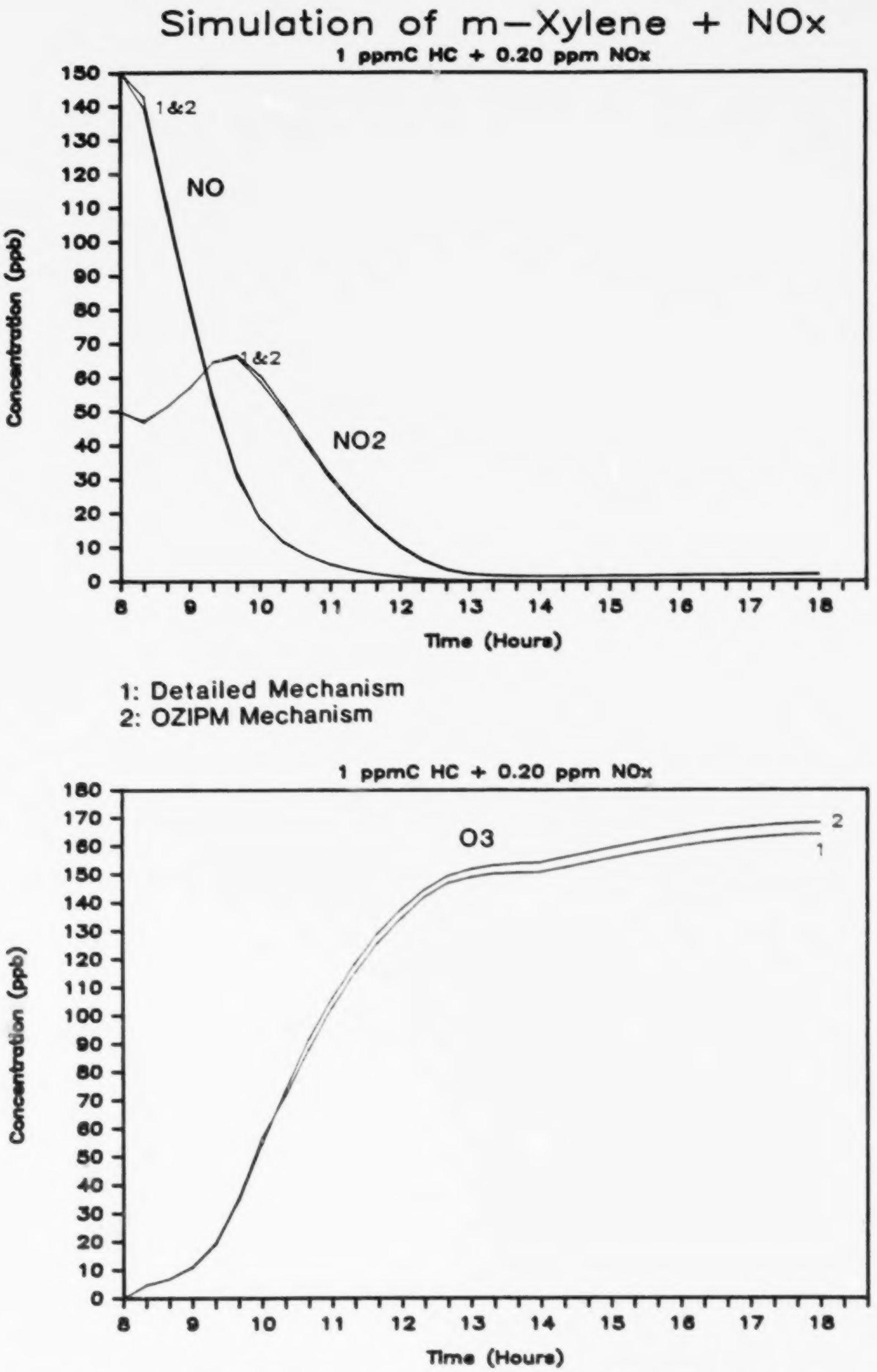


Figure 3-9. Comparison of NO, NO_2, and O_3 predictions for 1 ppmC m-xylene + 0.20 ppm NO_x with detailed and OZIPM mechanism.

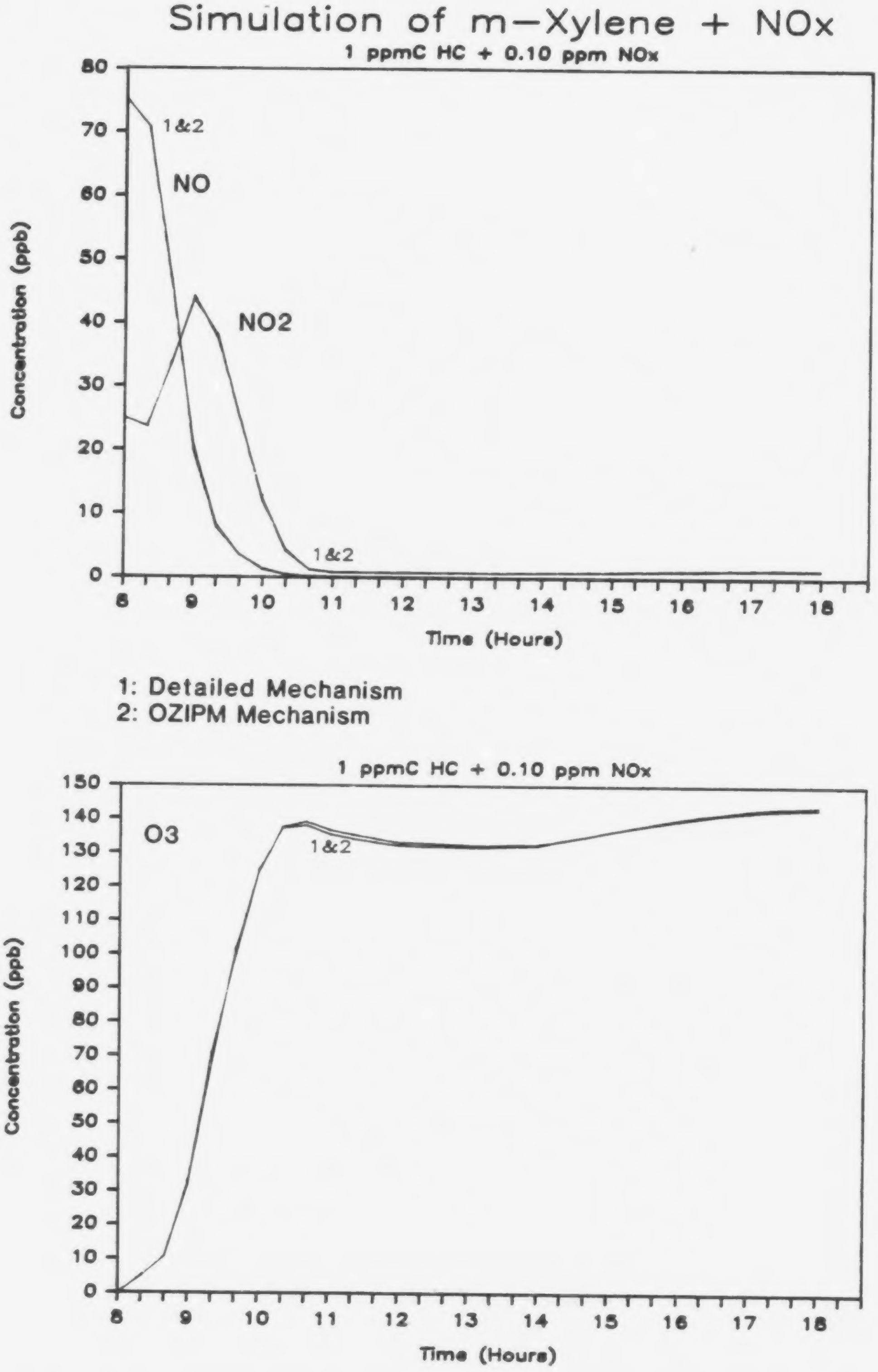


Figure 3-10. Comparison of NO, NO_2, and O_3 predictions for 1 ppmC m-xylene + 0.10 ppm NO_x with detailed and OZIPM mechanism.

The actual methyl ethyl ketone oxidation mechanism involves numerous peroxy radicals. The detailed mechanism, shown in Table 2-2, has some lumping of these RO_2 radicals. Further lumping was performed for the OZIPM mechanism by combining MKO_2 with the other RO_2 type radicals, as shown below.

Detailed:

$$\begin{aligned}
\mathrm{MEK} + \mathrm{OH} &\longrightarrow \mathrm{R2O2} + .5\mathrm{MKO2} + 1.5\mathrm{RO2} + .5\mathrm{ALD2} \\
&\qquad + .5\mathrm{MCO3} + .5\mathrm{RCO3} \\
\mathrm{MKO2} + \mathrm{NO} &\longrightarrow \mathrm{NO2} + \mathrm{HCHO} + \mathrm{PCO3} + \mathrm{RCO3} \\
\mathrm{MKO2} + \mathrm{HO2} &\longrightarrow \mathrm{ROOH} + \mathrm{HCHO} + \mathrm{ALD2} \\
\mathrm{MKO2} + \mathrm{RO2} &\longrightarrow .5\mathrm{HO2} + \mathrm{HCHO} + \mathrm{ALD2} + \mathrm{RO2} \\
\mathrm{MKO2} + \mathrm{RCO3} &\longrightarrow .5\mathrm{HO2} + \mathrm{HCHO} + \mathrm{ALD2} + \mathrm{RCO3}
\end{aligned}$$

Condensed:

$$\begin{aligned}
\mathrm{MEK} + \mathrm{OH} &\longrightarrow 1.5\mathrm{R2O2} + 1.5\mathrm{RO2} + .5\mathrm{ALD2} + .5\mathrm{MCO3} \\
&\qquad .5\mathrm{HCHO} + .5\mathrm{PCO3} + \mathrm{RCO3}
\end{aligned}$$

The influence of this change was investigated in pure MEK-NO_x simulations. The modification has essentially no effect on the predictions.

The last area of condensation for the OZIPM mechanism was in the higher alkene chemistry. The detailed mechanism includes four higher alkenes: propene, 1-butene, trans-2-butene, and iso-butene. Since the >C2 alkenes rarely comprise more than 10% or 15% of NMOC emissions in urban areas, it was appropriate to investigate reducing the number of alkene precursor species. Comparisons of the propene and 1-butene mechanism predictions were made for cases with 1 ppmC NMOC and 0.33 and 0.20 ppm NO_x. Other conditions for the simulations are shown on Table 3-6. The results, shown in Figures 3-11 and 3-12, indicate that the propene mechanism oxidizes NO_x faster and produces more ozone than the 1-butene mechanism. The ozone yields are 9 and 21% higher for propene than 1-butene in the 0.20 and 0.33 ppm NO_x cases, respectively.

Similar simulations were carried out to compare the trans-2-butene and isobutene mechanism. The results, shown in Figures 3-13 and 3-14, indicate that trans-2-butene oxidizes NO_x almost twice as fast as isobutene. This results in significantly different NO, NO_2, and ozone concentration profiles. For example, the maximum NO_2 concentration

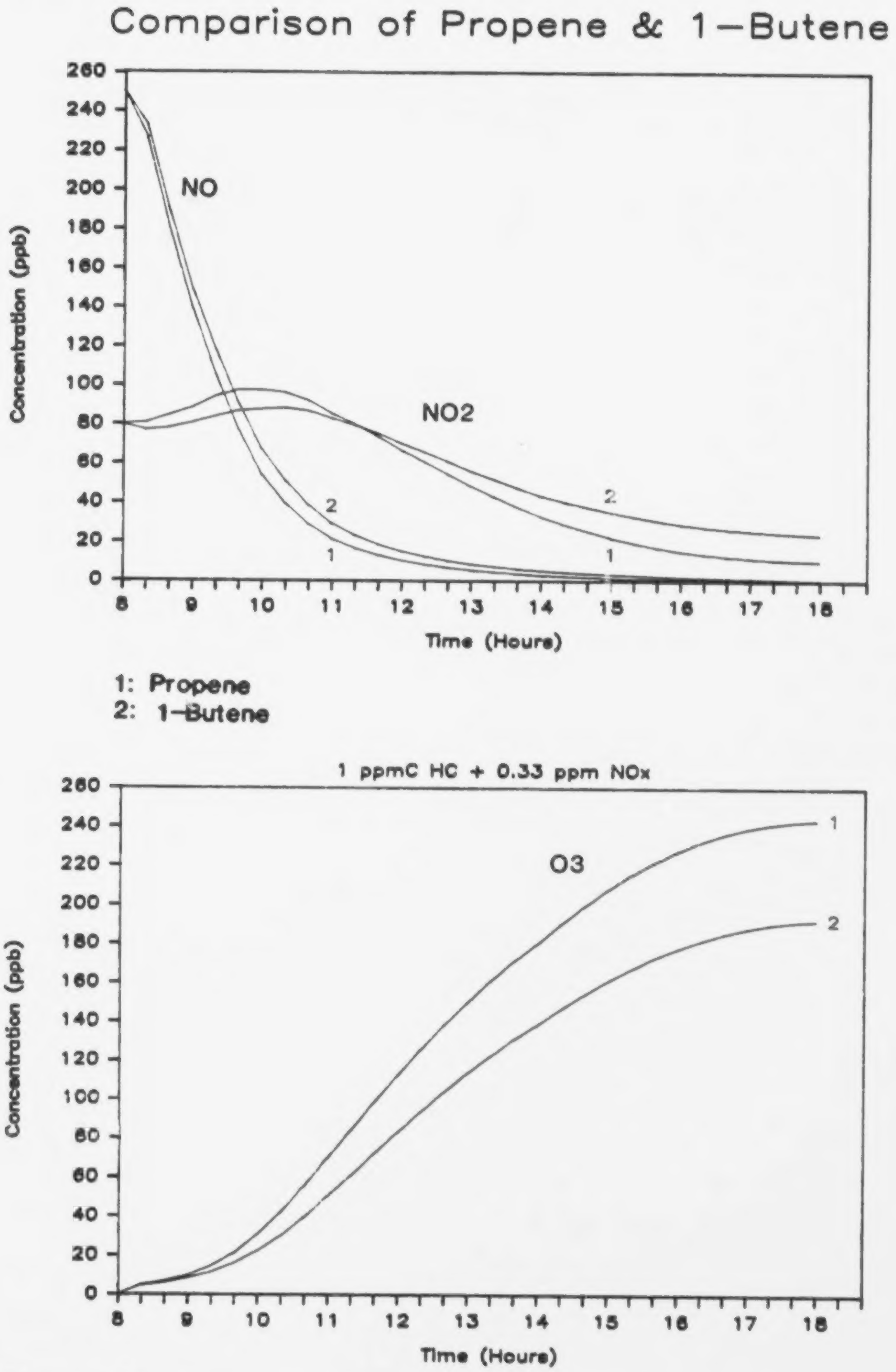


Figure 3-11. Comparison of NO, NO_2, and O_3 predictions with 1 ppmC propene and 1 ppmC 1-butene at $NMOC/NO_x = 3$.

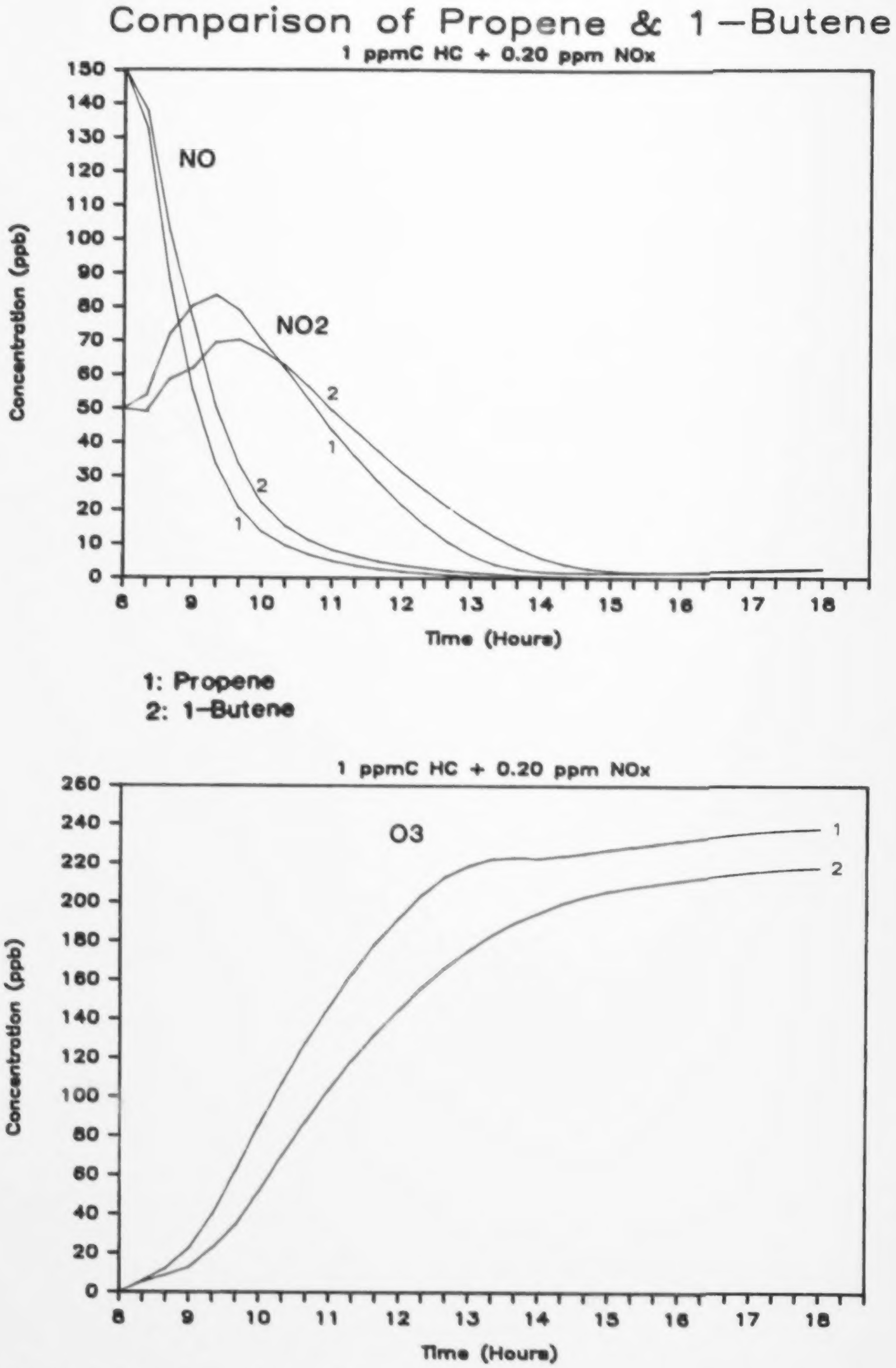


Figure 3-12. Comparison of NO, NO_2, and O_3 predictions with 1 ppmC propene and 1 ppmC 1-butene at $NMOC/NO_x = 5$

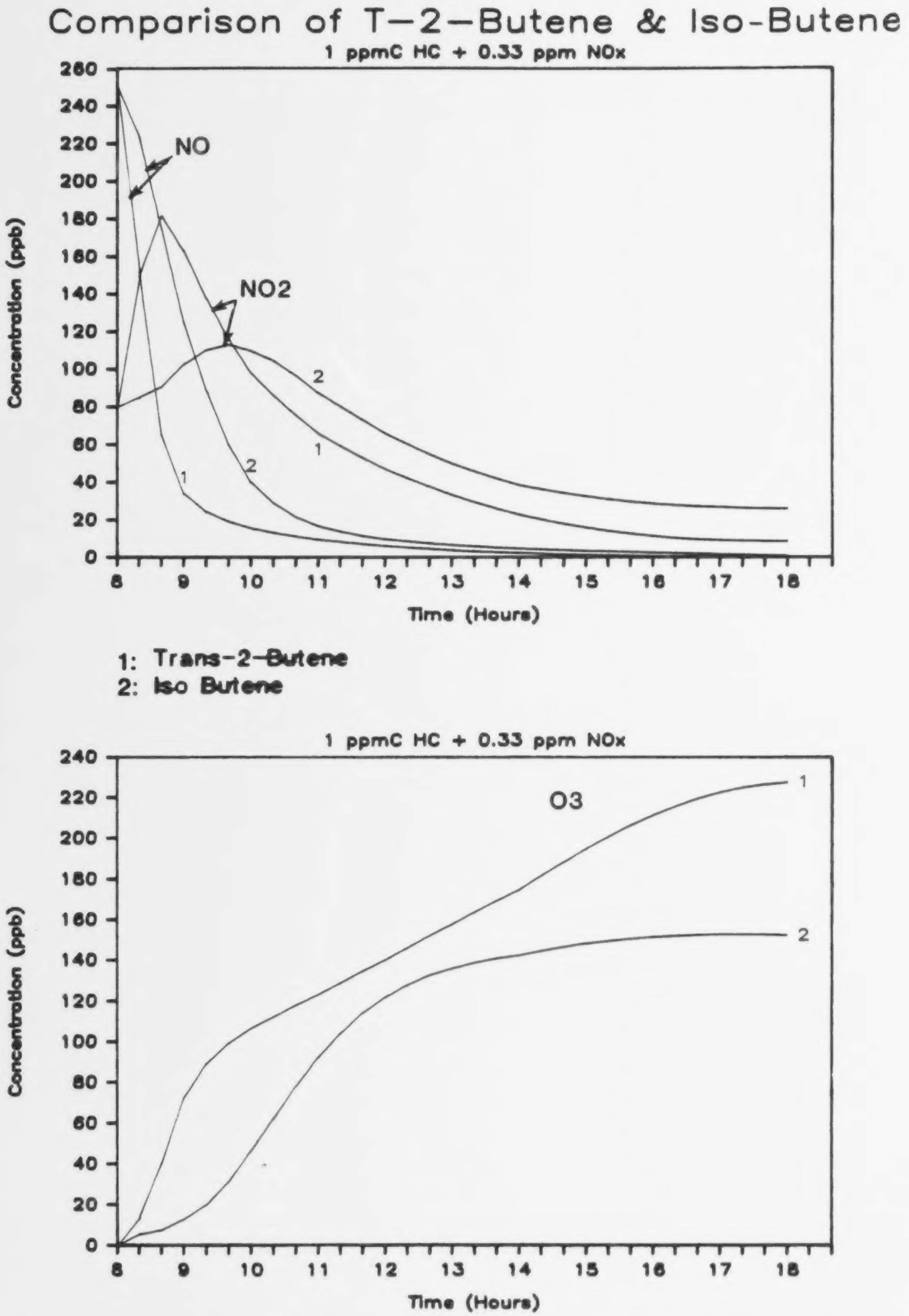


Figure 3-13. Comparison of NO, NO_2, and O_3 predictions with 1 ppmC trans-2-butene and 1 ppmC iso-butene at $NMOC/NO_x = 3$.

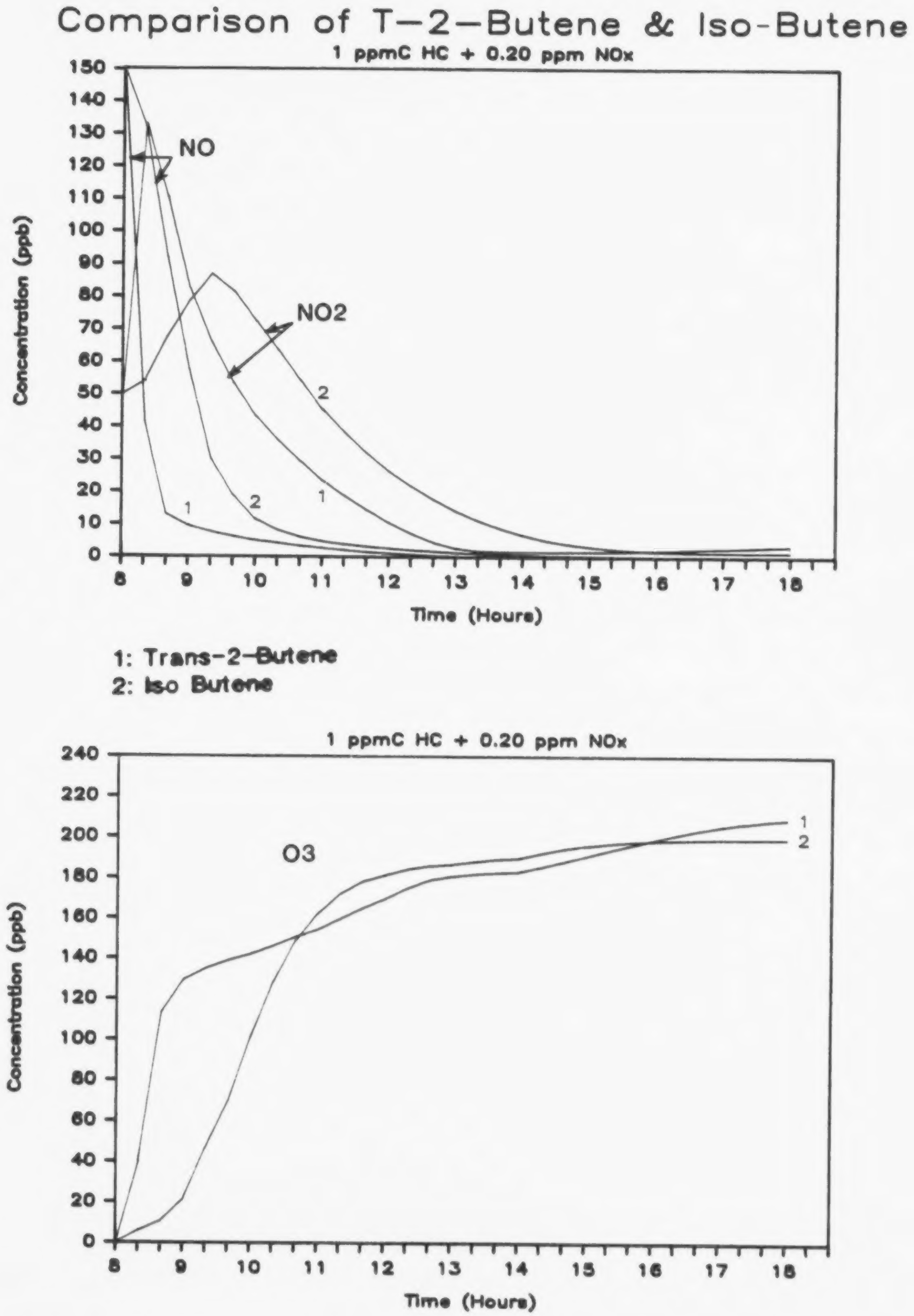


Figure 3-14. Comparison of NO, NO_2, and O_3 predictions with 1 ppmC trans-2-butene and 1 ppmC iso-butene at $NMOC/NO_x = 5$.

occurs one hour earlier with the trans-2-butene mechanism than with the isobutene mechanism. The differences in the concentrations early in the runs are somewhat exaggerated by the high dilution rates during this period; nevertheless, the differences are significant. The figures show that ozone is produced much more rapidly with the trans-2-butene mechanism. While the ozone yields in the cases with 0.20 ppm NO_x are comparable with both mechanisms, the ozone yield in the runs with higher NO_x (0.33 ppm) are 32% higher with the trans-2-butene mechanism than the isobutene mechanism. These differences are consistent with the differences in the reactivity of the products of the two alkenes. A significant portion of the isobutene is oxidized to ketones which are significantly less reactive than the aldehydes produced from trans-2-butene oxidation.

Although there are significant differences in the chemistry of the higher alkenes, it is difficult to justify using more than two higher alkene species in the OZIPM mechanism because they are usually a small fraction of NMOCs. It was decided to use the same surrogate alkene species in the OZIPM mechanism as employed in the Atkinson et al. (1982) mechanism. With this approach, all terminal alkenes are represented by propene and all internal alkenes are represented by trans-2-butene. The rationale for choosing these species was that they are good representatives of moderately fast-reacting and very fast-reacting species. In addition, the propene mechanism has been tested more extensively than any other portion of the mechanism.

3.2 The Condensed Mechanism

As previously discussed, it is necessary to represent the chemistry with fewer species in mechanisms intended for use in multi-cell models. The condensed mechanism developed here incorporates all the approximations made in the OZIPM mechanism plus additional lumping of organics and elimination of less important species. The justification for most of the condensation steps is that they do not appear to significantly affect the predictions when the mechanism is applied to problems involving urban mixtures of organics.

Several species that contribute little to the overall reactivity of mixtures were eliminated from the condensed mechanism. The reactions of acetone (ACET) were eliminated because its chemical half-life is more than four days under typical urban conditions and, although significant amounts of acetone are formed from alkanes, they do not contribute much reactivity. The reactions of phenols (PHEN) were also eliminated. The phenols react fairly fast during the day and night; however, the amount of phenols formed is very small relative to other reactive products of the aromatics.

Glyoxal (GLYX) also contributes little to the overall reactivity of urban mixtures; however, it is probably inappropriate to entirely ignore its reactions. Formaldehyde and carbon monoxide were substituted for glyoxal in the condensed mechanism. This approximation probably slightly overestimates glyoxal's contribution to reactivity. This substitution has the advantage that it also eliminates the acyl peroxy radical (GCO3) and PAN analog (GPAN) formed from glyoxal. Simulations of urban conditions with the detailed mechanism indicated that the maximum GPAN concentrations accounted for less than 0.2 percent of the nitrogen in the system, so elimination of the PAN analog is insignificant.

There are several other products in the mechanism, such as nitric acid, alkyl nitrates, hydrogen peroxide, and organic peroxides, which are fairly stable. The chemical half-lives for alkyl nitrates, H_2O_2, and organic peroxides range from 15 to 30 hours. The chemical half-life of nitric acid is considerably longer. Simulations were made to investigate the importance of the reactions of these species in hope that some or all could be ignored. The results indicated that, although the nitrogen-containing species react very slowly, their reactions produce small amounts of NO_2 and NO_3 that affect the ozone predictions late in the simulations after most of the NO and NO_2 are oxidized. Thus, the reactions of nitric acid and alkyl nitrates were kept in the condensed mechanism. Urban simulations made without the H_2O_2 and ROOH destruction reactions showed that these reactions had virtually no effect on the predictions of key species (NO, NO_2, O3, and organic decay rates). Although these reactions produce a significant amount of radicals, the radical production occurs mostly after the NO_x is totally consumed so that the radicals have little effect on the key species. Thus, H_2O_2 and ROOH were eliminated from the species list.

Further condensation of the higher aldehydes was incorporated into the condensed mechanism. Acetaldehyde (ALD2) was substituted for propionaldehye (RCHO) on a mole (not carbon) basis. The acyl peroxy radical associated with acetaldehyde (MCO3) was substituted for the higher acyl peroxide radical (PCO3). This also eliminated the corresponding PAN analog, PPN, from the mechanism. The rationale for this approximation is that the RCHO, PCO3, and PPN reactions are almost identical to the ALD2, MCO3, PAN reactions, and that it makes little difference in predictions for key species in urban simulations. However, it is important to recognize that this approximation and others in the condensed mechanism make it more difficult to compare the condensed mechanism's predictions to ambient observations of aldehydes and PAN, since the species in the model are truly lumped species.

The last and most significant condensation of the mechanism involved separately combining the classes of alkanes, higher alkenes, and higher aromatics. The C4-C5 and >C5 alkanes are combined into a single >C3 alkanes classes (ALKA). The internal and terminal alkenes are represented as a single class of higher alkenes (ALKE). The di-alkylbenzenes and tri-alkylbenzenes are represented by a single higher aromatics class (AROM). The reaction rates and products for the combined classes are mole-weighted functions of the detailed reactions. Since the VOC splits for these classes may vary significantly in different applications, the mechanism shown in Table 3-4 has the rate constants and product coefficient expressed as functions of the splits between the two alkane, two higher alkene, and two higher aromatic classes. The recommended default splits for urban areas are

C4-C5 Alkanes Fraction of >C3 Alkanes	0.43
Terminal Alkenes Fraction of Higher Alkenes	0.60
Di-alkylbenznes Fraction of Higher Aromatics	0.60

on a carbon basis. The default average number of carbons per molecule are 5.92, 3.4, and 8.4 for the lumped alkanes, higher alkene, and higher aromatic classes, respectively. The default rate constants and product coefficients at 298°K for the six lumped reactions are shown as follows:

ALKA + OH —> .112 HCHO +.380 ALD2 +.643 MEK +.131 RO2N
+.868 RO2R +.698 R2O2 +.157 RO2

k = 6740 per ppm-min (or 4.56E-12 molecules/cc-sec)

ALKE + OH —> .667 HCHO +1.33 ALD2 + RO2R + RO2
k = 57300 per ppm-min (or 3.88E-11 molecules/cc-sec)

ALKE + O3 —> .427 HCHO +.667 ALD2 +.177 RO2R +.177 RO2
+.183 HO2 + .08 OH +.187 CO
k = 0.110 per ppm-min (or 7.42E-17 molecules/cc-sec)

ALKE + O —> .333 CO +.333 MEK +.267 HCHO +.133 ALD2
+.267 HO2 + .40 RO2R + .40 RO2
k = 15400 per ppm-min (or 1.04E-11 molecules/cc-sec)

ALKE + NO3 —> NO$_2$ +.667 HCHO +1.33 ALD2 + R2O2 + RO2
k = 194 per ppm-min (or 1.31E-13 molecules/cc-sec)

AROM + OH —> .17 CRES + .17 HO2 + .83 RO2R + .83 RO2
+.59 DIAL +.518 MGLY +.597 HCHO +.597 CO
k = 56800 per ppm - min (or 3.84E-11 molecules/cc-sec)

These default values should be used only if better data are not available. The recommended approach for using the mechanism is to calculate the rate constants and product coefficients from the formulae given in Table 3-4 based on the speciation of the NMOC emissions inventory being used in the model application.

3.3 Mechanism Comparison

The effects of the condensation approximations were examined in numerous simulations. The detailed, OZIPM, and condensed mechanisms were applied to identical problems for the purpose of comparison. The first set of simulations involved examining the alkene, alkane, and aromatic chemistry separately. The simulations were initialized with 1 ppmC hydrocarbons and varying amounts of NO_x. The hydrocarbons in the alkene runs consisted of 23%, 46%, and 31% ethene, propene, and trans-2-butene, respectively, on a carbon basis. For the alkane runs, the hydrocarbons consisted of 43% and 57% C4-C5 and >C5 alkanes, respectively, on a carbon basis. For the aromatic runs, the hydrocarbons were represented as 62%, 23% and 15% toluene, m-xylene, and mesitylene, respectively, on a carbon basis. Other parameters input for the calculations are summarized in Table 3-7. Figure 3-15 shows the ozone predictions for the alkene/NO_x runs carried out at NMOC/NO_x ratios of 3 and 6. The predictions show excellent agreement for all three mechanisms. The rates of ozone formation are in good agreement, and the ozone yields are within 3%. Figure 3-16 shows the ozone results for alkane simulations carried out at NMOC/NO_x ratios of 10 and 20. The results show that the OZIPM and condensed mechanisms can predict the ozone concentrations within 1 and 4% of that predicted by the detailed mechanism, respectively, under these conditions. The condensed mechanism predicts slightly more ozone than the other mechanisms for this alkane mixture. Figure 3-17 shows the ozone profiles from aromatic runs at NMOC/NO_x ratios of 3 and 6. The timing is good in both cases. The ozone yields from the OZIPM mechanism are 1% and 4% higher than those from the detailed mechanism in the high and low NMOC/NO_x ratio cases, respectively. The ozone yields from the condensed mechanism are 4% and 12% higher than those from the detailed mechanism in the high and low NMOC/NO_x ratio cases, respectively. Hence, condensation has slightly increased the ozone yields from the aromatic mechanism.

The most important test of the mechanisms is to examine predictions obtained with surrogate organic mixtures. Simulations were carried out with 1 ppmC of a typical urban organic mixture and varying amounts of NO_x. The NO_x levels were set to achieve NMOC/NO_x ratios of 3, 6, 10, and 20. The low NMOC/NO_x ratio case is simulated for two diurnal cycles to test the nightime chemistry. The ozone predictions for these runs are shown in Figures 3-18 and 3-19. The level of agreement is excellent in all cases. The OZIPM mechanism's ozone predictions are within 2% of those from the detailed mechanism. The condensed mechanism's ozone

Table 3-7

Conditions for Mechanism Comparison Simulations

Solar Radiation Inputs:	
Place:	Los Angeles, CA
Lattitude:	34.
Longitude:	118.
Time Zone:	8.
Date:	June 21, 1986
Photolysis Rates:	Table 2-4
Mixing Heights:	250 m at 0600 Hours
	250 m at 0800 "
	390 m at 0900 "
	565 m at 1000 "
	729 m at 1100 "
	850 m at 1200 "
	937 m at 1300 "
	1000 m at 1400 "
	1000 m at 2000 "
Temperature:	30 C
Ozone aloft:	0.08 ppm
NMOC aloft:	0.05 ppmC
Initial Values:	[CO] = 1 ppm [O3] = 0.01 ppb [H2O] = 20,000 ppm
NO/NOx Ratio:	0.75
NMOC/NOx:	3, 6, 10, 20
NMOC Composition:	Table 4-7
Post 6 AM Emissions:	None

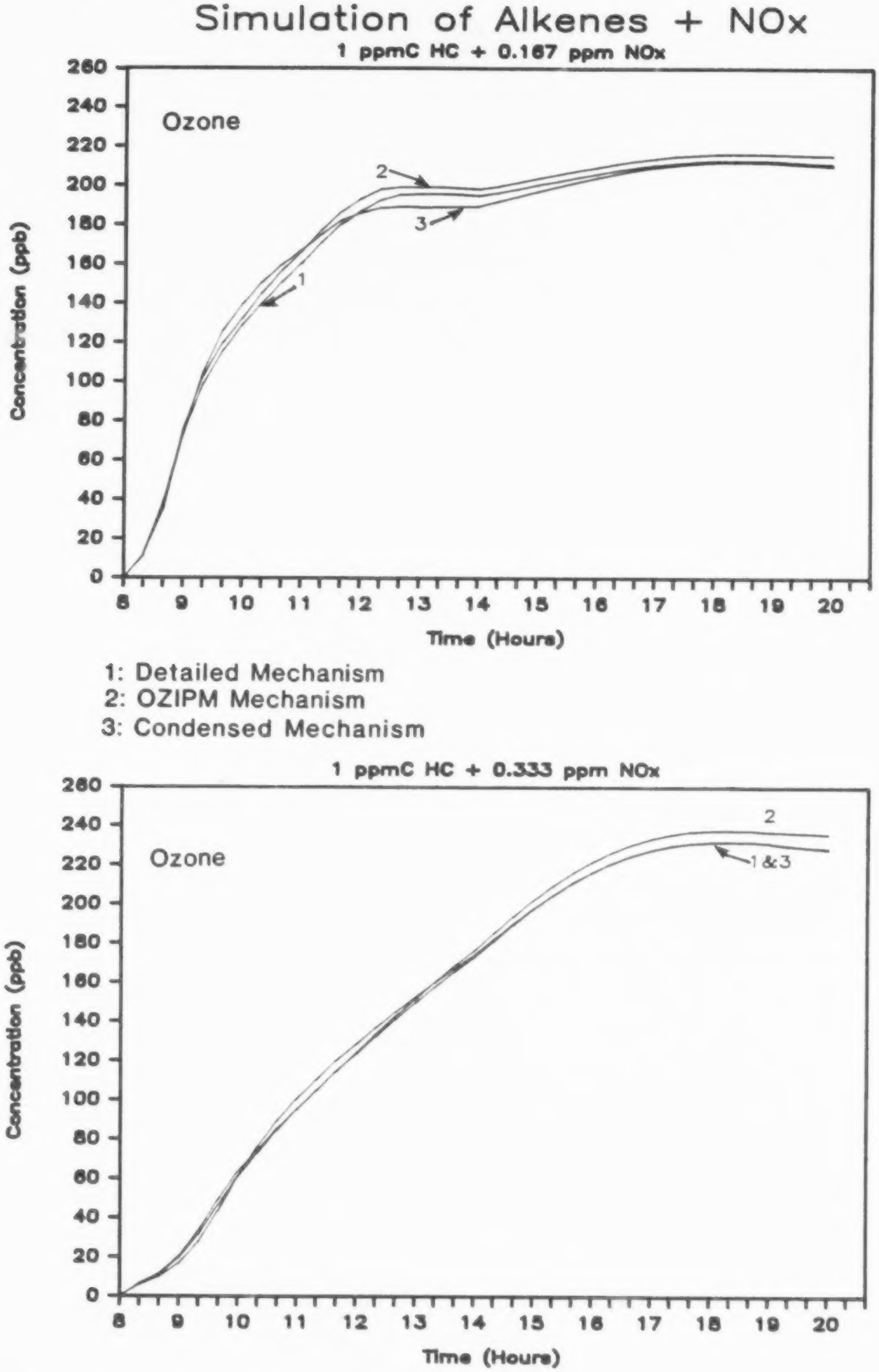


Figure 3-15. Comparison of ozone predictions from the three mechanisms for mixed alkenes and NO_x at $NMOC/NO_x$ = 3 and 6.

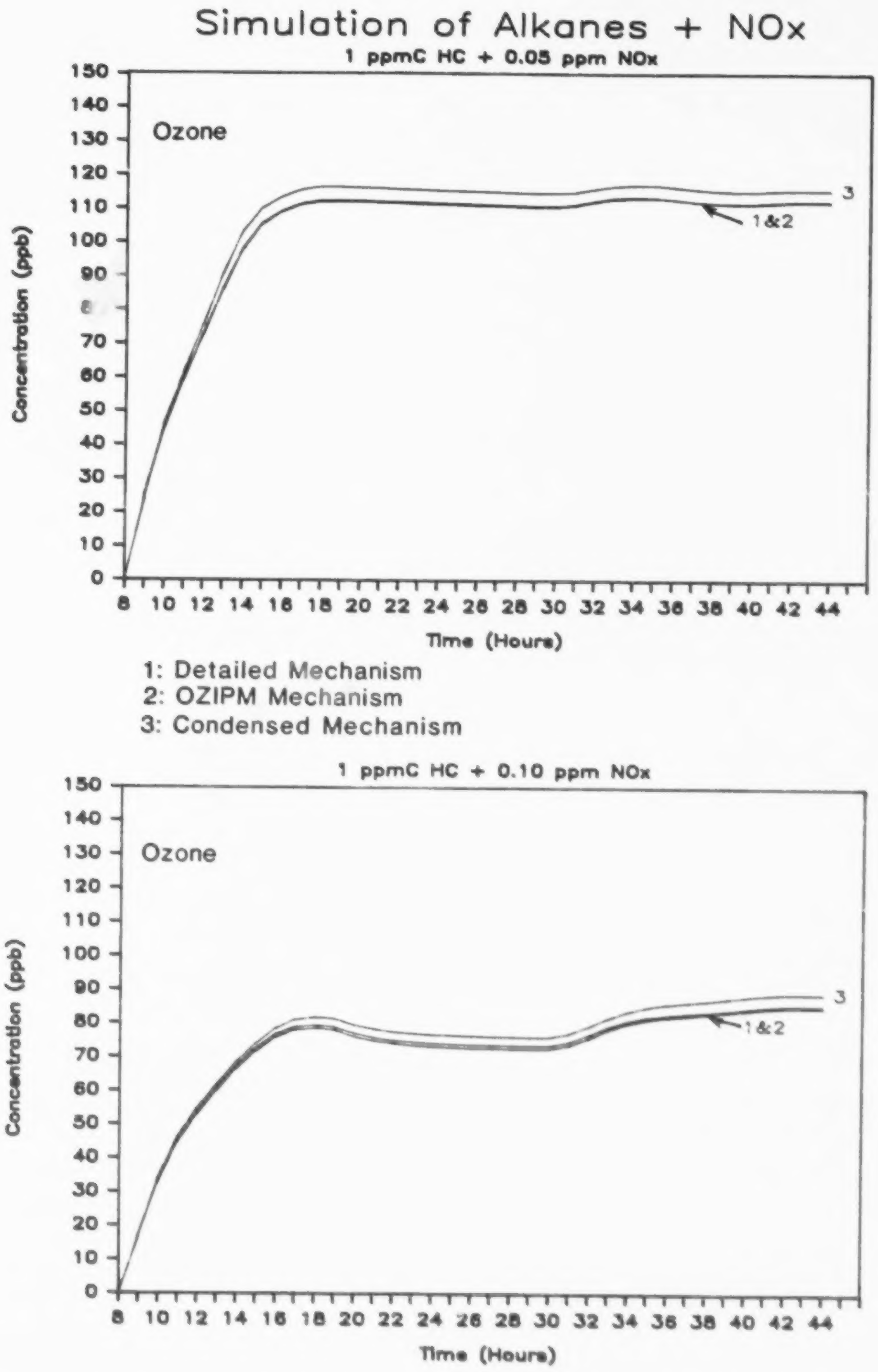


Figure 3-16. Comparison of ozone predictions from the three mechanisms for mixed alkanes and NO_x at $NMOC/NO_x$ = 10 and 20.

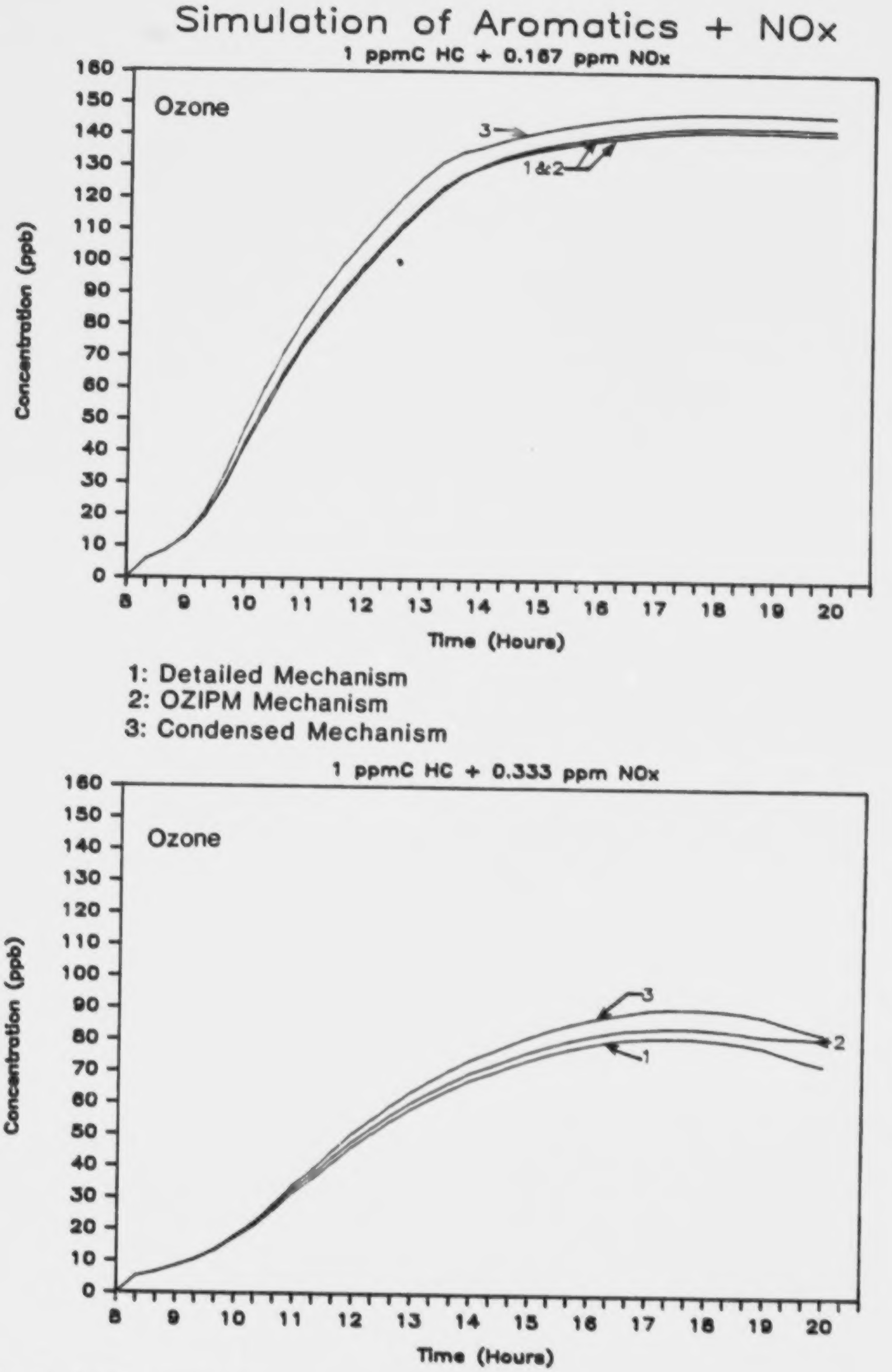


Figure 3-17. Comparison of ozone predictions from the three mechanisms for mixed aromatics and NO_x at $NMOC/NO_x = 3$ and 6.

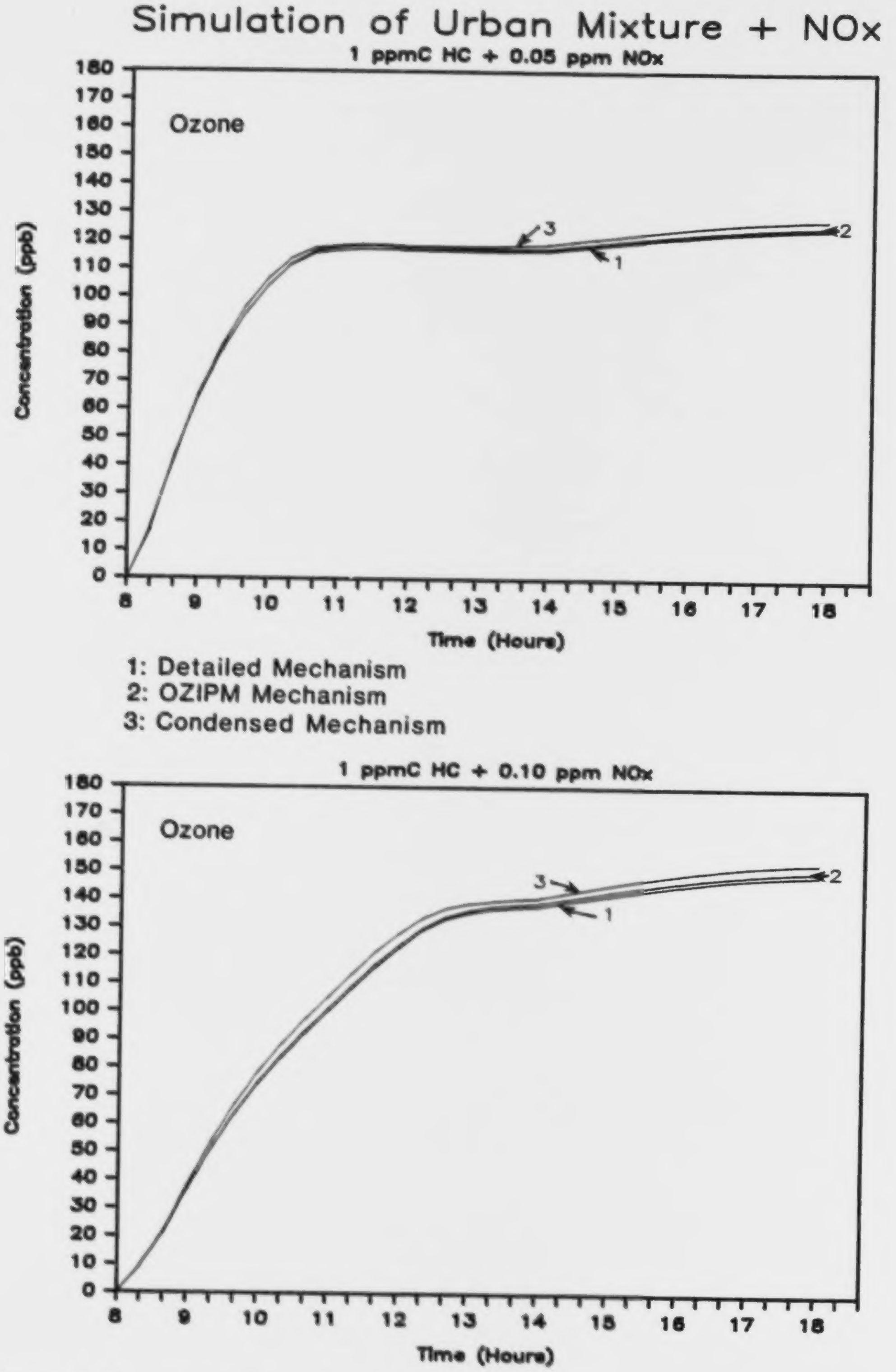


Figure 3-18. Comparison of ozone predictions from the three mechanisms for an urban NMOC mixture at $NMOC/NO_x$ = 10 and 20.

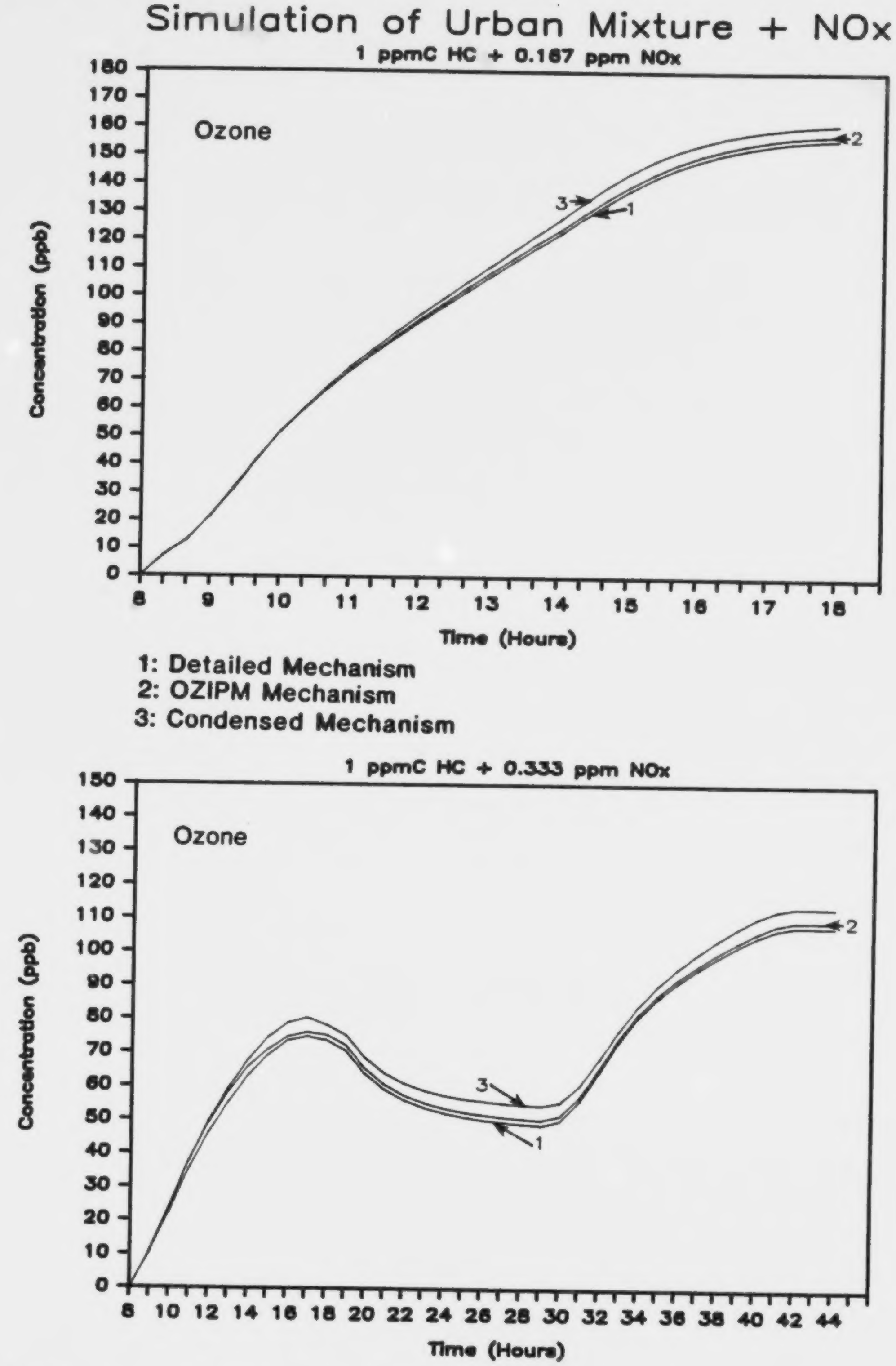


Figure 3-19. Comparison of ozone predictions from the three mechanisms for an urban NMOC mixture at NMOC/NO_x = 3 and 6.

predictions are 1% to 5% higher than those from the detailed mechanism for these conditions.

Similar runs were carried out to investigate the performance of the mechanisms at alternate temperatures. Figure 3-20 shows the ozone prediction in a case with an NMOC/NO_x ratio of 3 at 10°C and 40°C instead of 25°C. The level of agreement between the three mechanisms is not quite as good at these alternate temperatures; however, the largest discrepancy is still less than 5% and 13% for the OZIPM and condensed mechanisms, respectively, in these two-day runs.

This level of agreement between the mechanisms can only be achieved if the rates of NO_x and NMOC oxidation and radical concentrations are similar among the mechanisms. Figures 3-21 through 3-28 compare the predictions for NO, NO_2, nitric acid, PANs, ethene, higher alkenes, toluene, higher aromatics, alkanes, MEK, hydrogen peroxide, HO_2, RO_2, and OH for the urban mixture case with an initial NMOC/NO_x ratio of six. The agreement between the OZIPM and detailed mechanisms is excellent (i.e., within ±2%) for all species. The agreement between the condensed and detailed mechanisms is within about 10% for all species except the radicals. The condensed mechanism predicts maximum HO_2, OH, and RO_2 concentrations that are 15% to 20% higher than those predicted by the detailed mechanism for these conditions. Considering that the condensed mechanism has only about half the number of integrated species as the detailed mechanism, this level of agreement is considered acceptable.

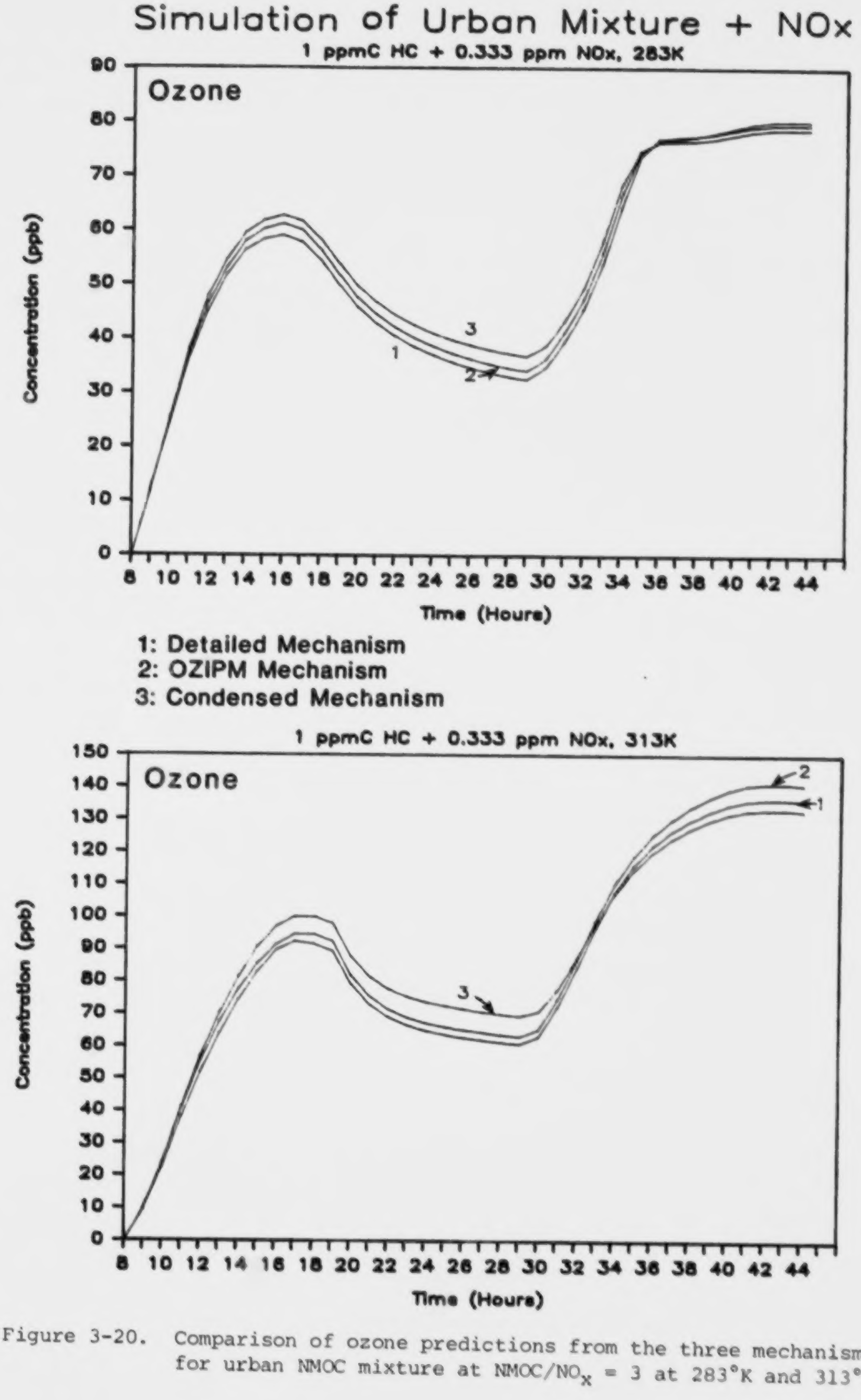


Figure 3-20. Comparison of ozone predictions from the three mechanisms for urban NMOC mixture at $NMOC/NO_x = 3$ at 283°K and 313°K.

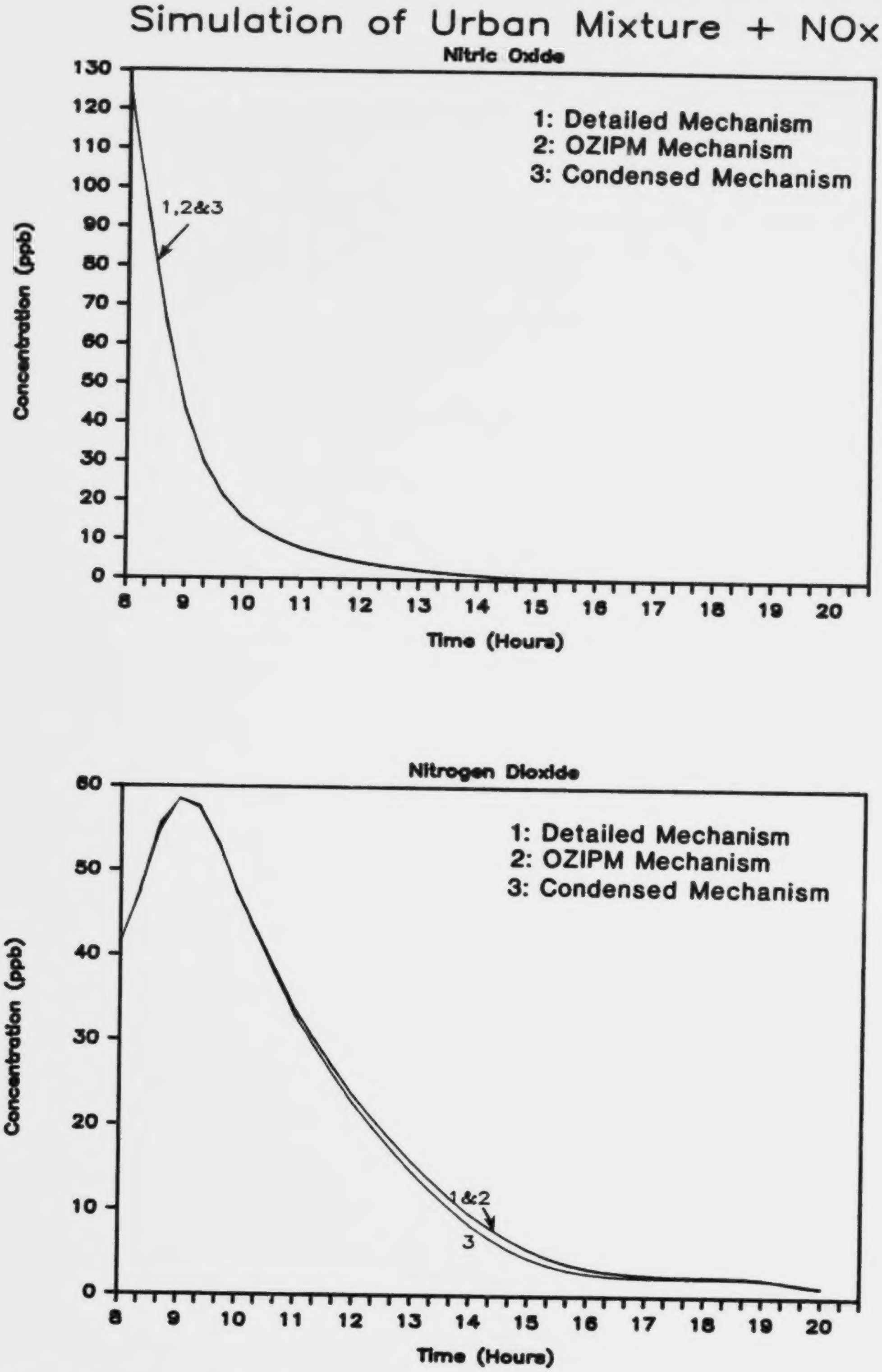


Figure 3-21. Comparison of NO and NO_2 predictions from the three mechanisms for an urban NMOC mixture at $NMOC/NO_x = 6$.

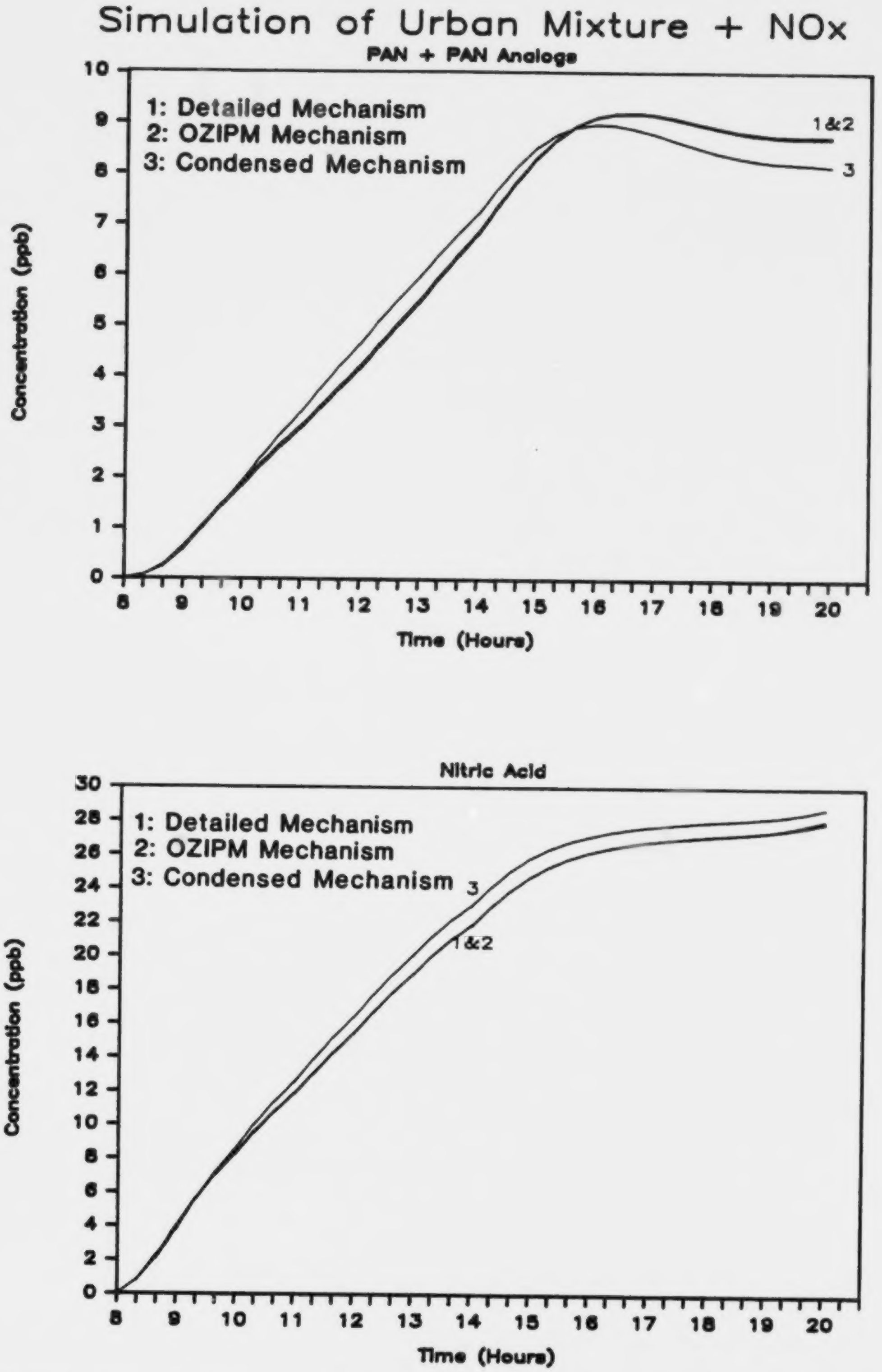


Figure 3-22. Comparison of PAN + PAN analogs and HNO_3 predictions from the three mechanisms for an urban NMOC mixture at $NMOC/NO_x = 6$.

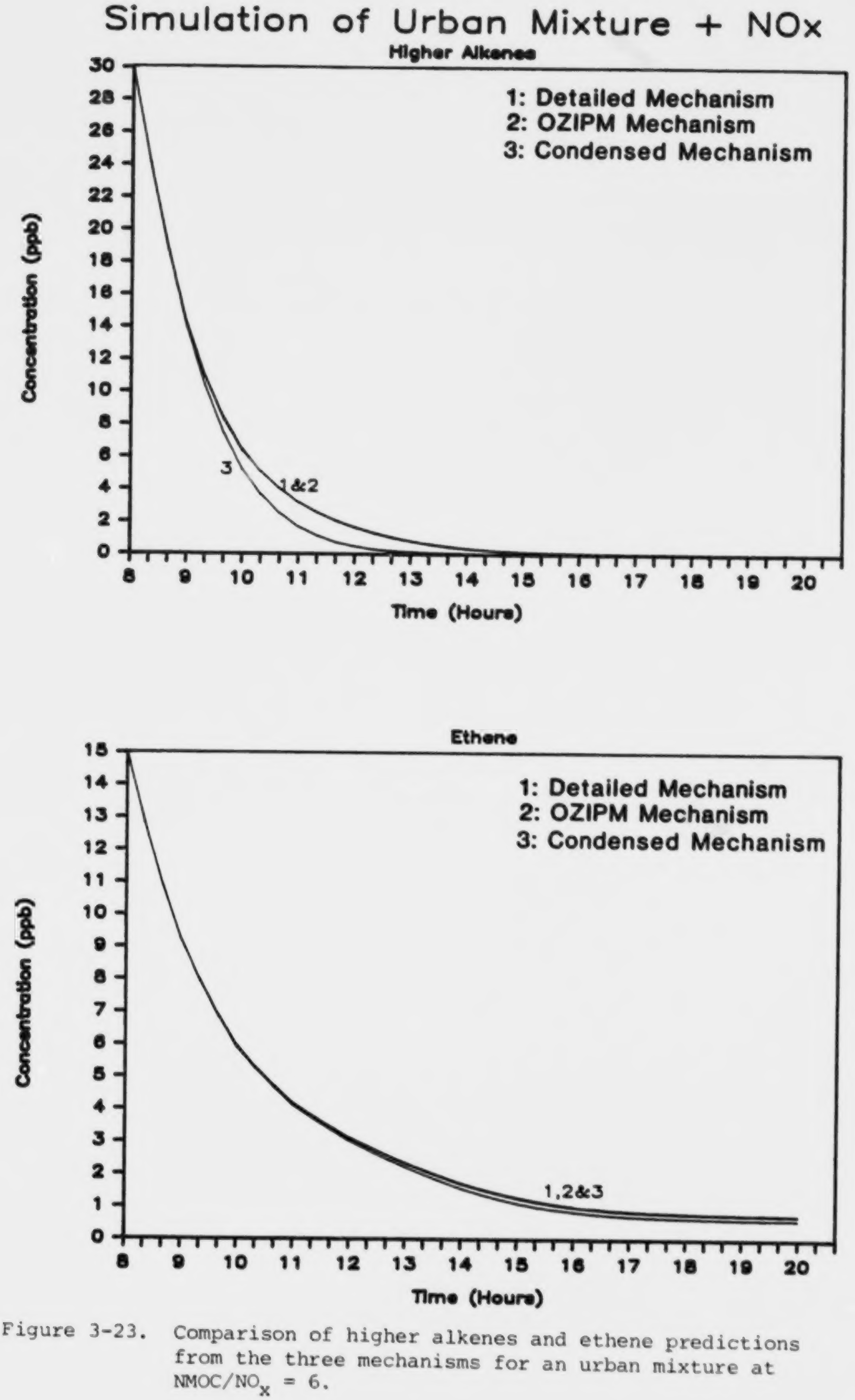


Figure 3-23. Comparison of higher alkenes and ethene predictions from the three mechanisms for an urban mixture at $NMOC/NO_x = 6$.

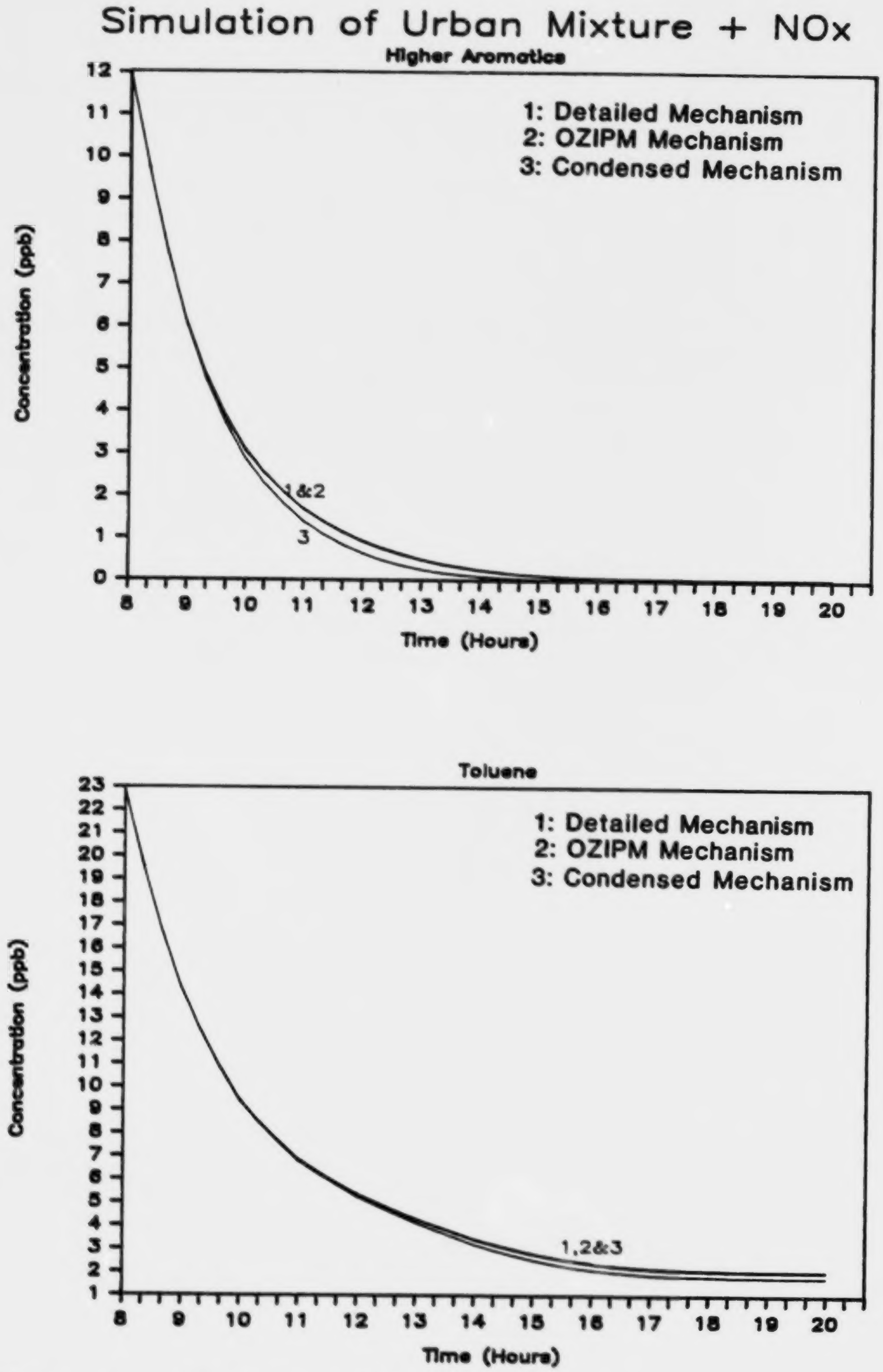


Figure 3-24. Comparison of higher aromatics and toluene predictions from the three mechanisms for an urban NMOC mixture at $NMOC/NO_x$ = 6.

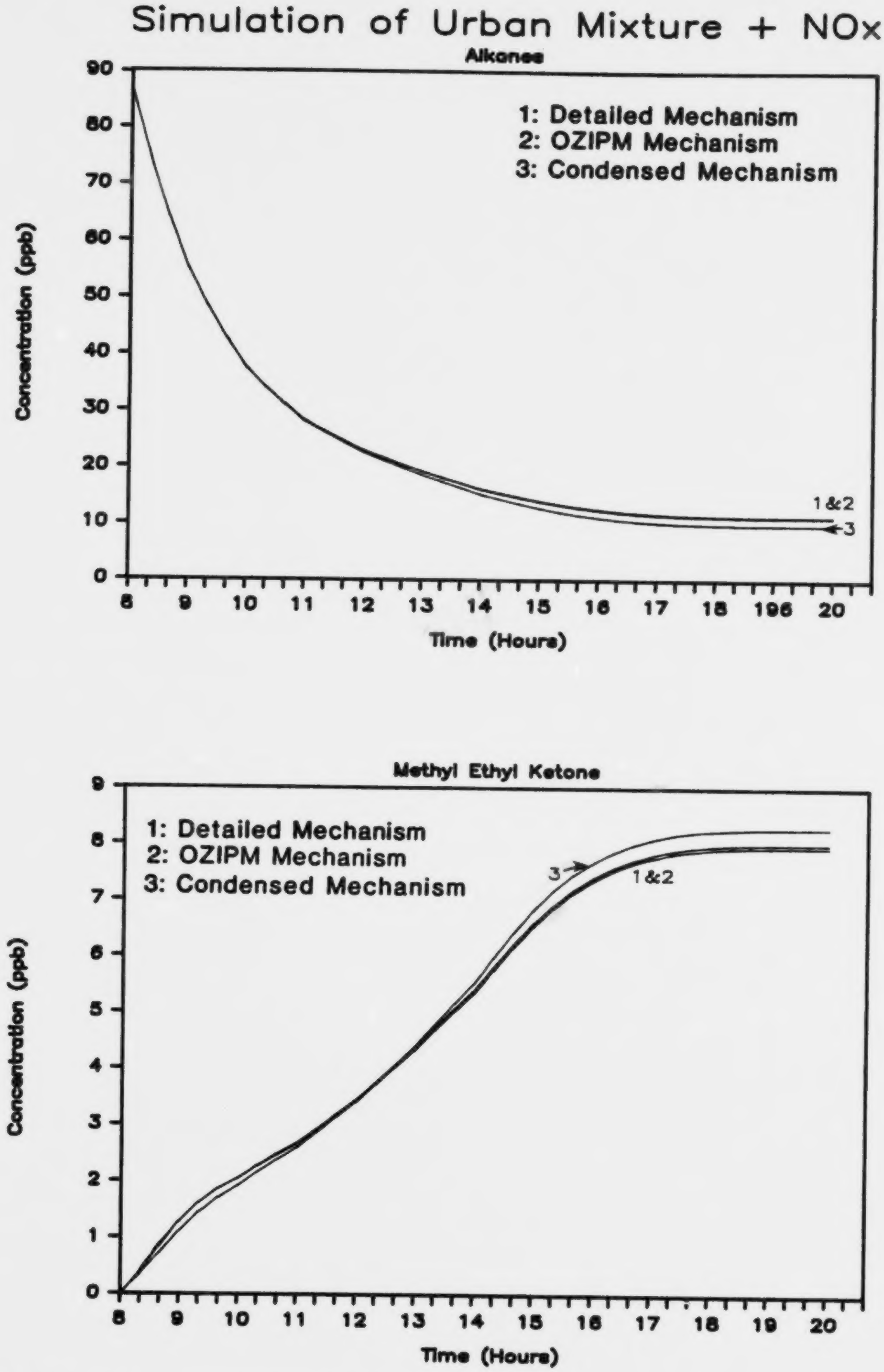


Figure 3-25. Comparison of alkanes and MEK predictions from the three mechanisms for an urban NMOC mixture at NMOC/NO_x = 6.

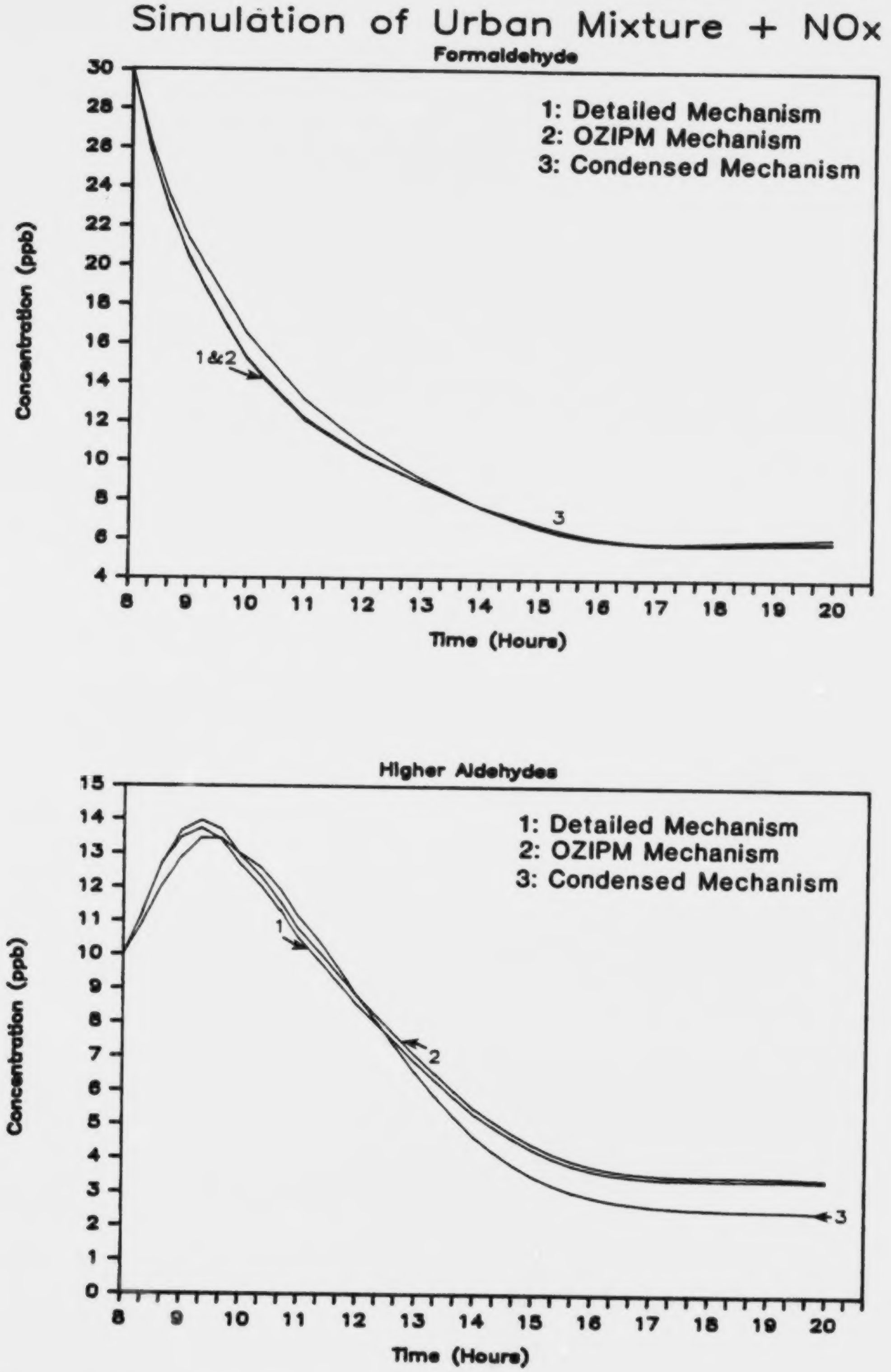


Figure 3-26. Comparison of formaldehyde and higher aldehyde predictions from the three mechanisms for an urban NMOC mixture at NMOC/NO_x = 6.

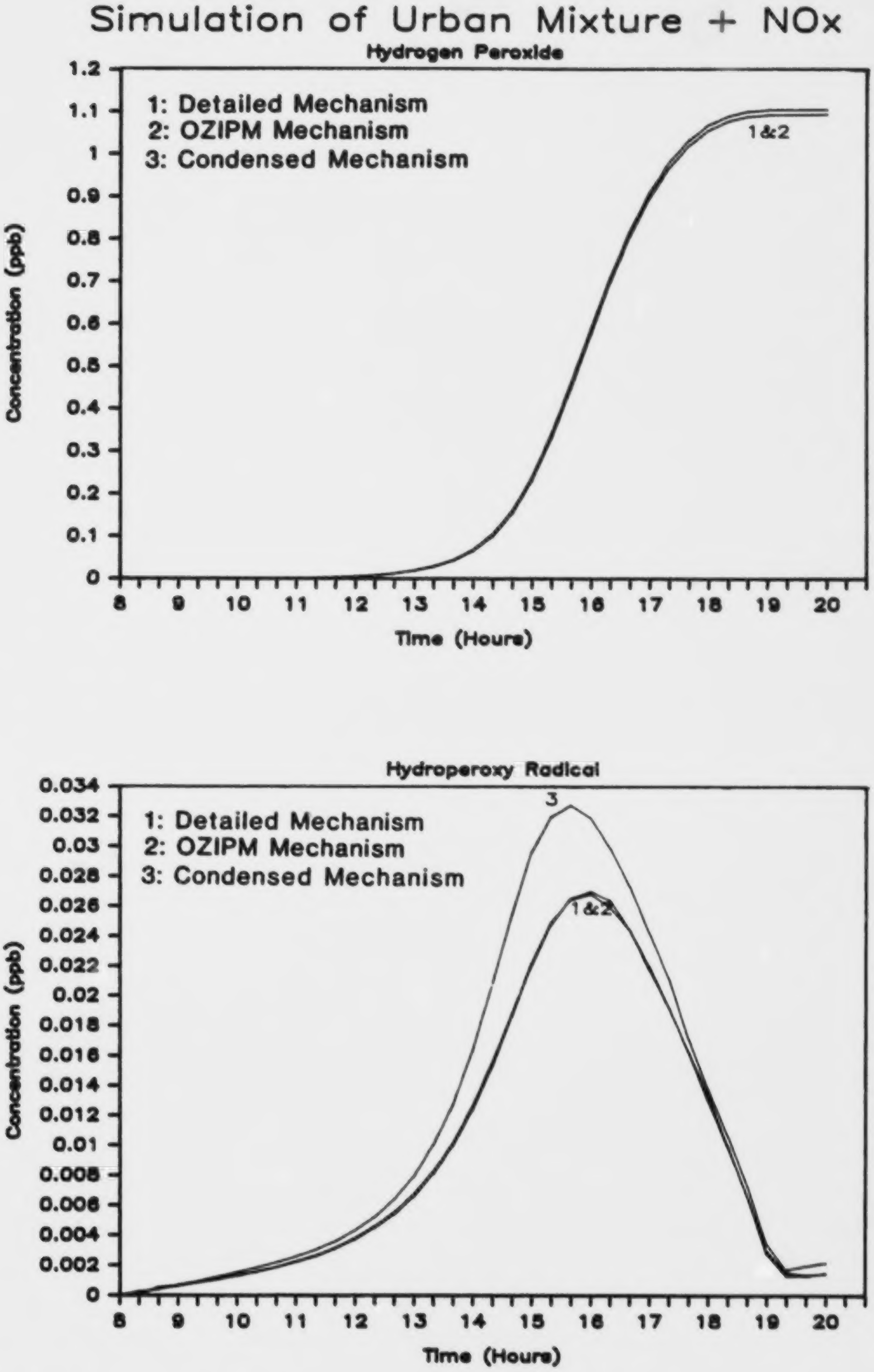


Figure 3-27. Comparison of H_2O_2 and HO_2 radical predictions from the three mechanisms for an urban NMOC mixture at NMOC/NO_x = 6.

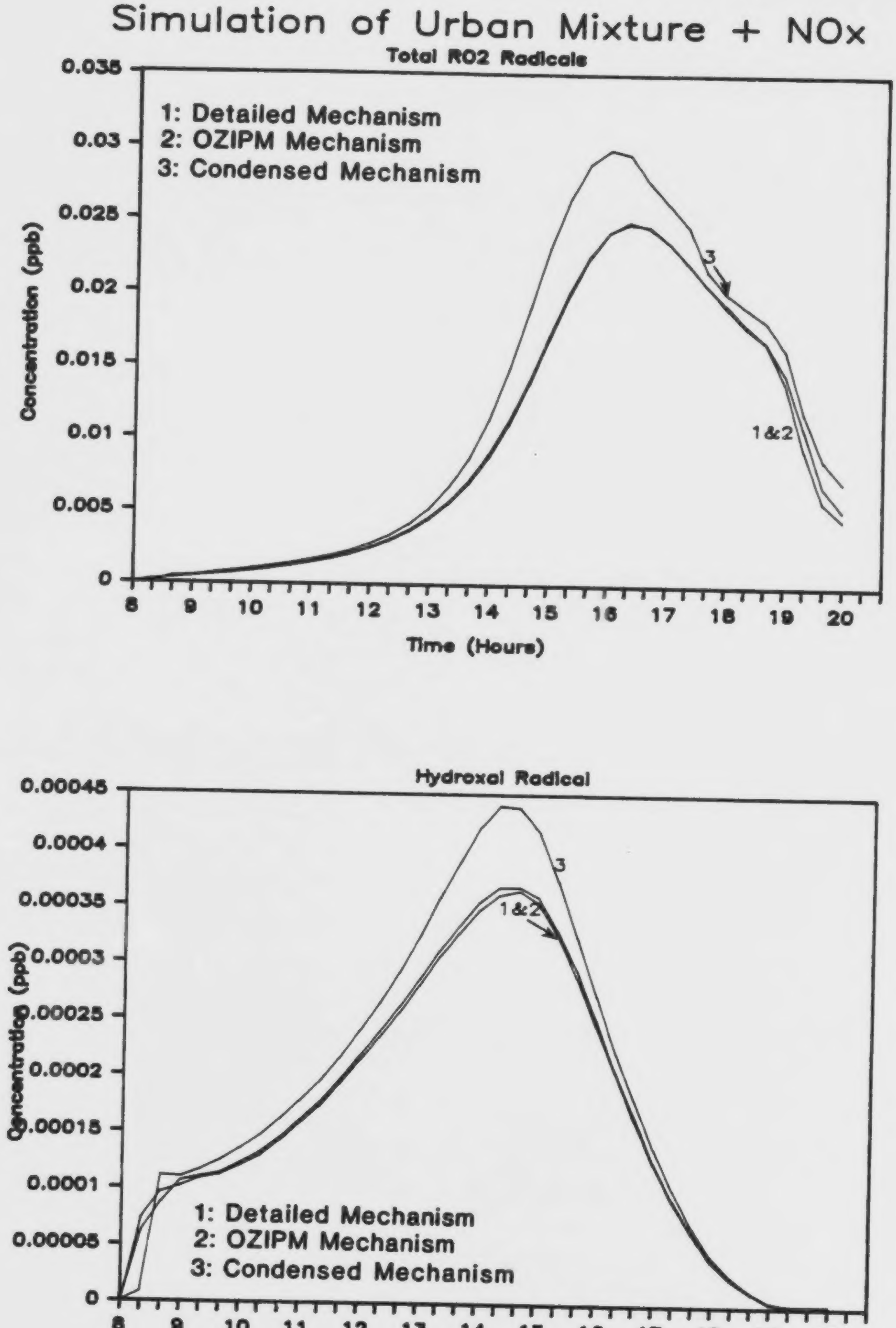


Figure 3-28. Comparison of RO_2 and OH radical predictions from the three mechanisms for an urban NMOC mixture at $NMOC/NO_x = 6$.

4. SPECIATION OF ORGANIC COMPOUNDS

Knowledge of NMOC speciation is essential for modeling urban ozone air quality with up-to-date chemical mechanisms. Most photochemical air quality simulation models require NMOC speciation information for emissions, initial concentrations, and boundary concentrations. The speciation data needs to be compiled using the NMOC classification scheme that is used by the specific mechanism incorporated into the simulation model. The NMOC classes in the the SAPRC/ERT OZIPM mechanism are shown in Table 4-1. Also shown in the table are the molecular weights and number of carbons per molecule of the surrogate species used to represent each class of compounds. Photochemical models require this information to convert concentrations and emissions from mass and molar carbon units to molar units.

The classification scheme shown in Table 4-1 is also recommended for the initial compilation of data for use with the condensed mechanism since proper use of that mechanism requires knowledge of the splits between the two alkane classes, the two higher alkene classes, and the two higher aromatic classes. Final inputs for the condensed mechanism should be classified into the classes shown in Table 4-2.

4.1 Assignment of Individual Species to Classes

The assignment of individual organic species to the organic classes in the OZIPM mechanism is shown in Table 4-3. Given detailed chemical speciation for either emissions or ambient concentrations, the individual species should be classified according to the assignments shown in the table. Unlike the Carbon Bond approach, where almost all species are divided into two or more classes, all of the carbon in individual species is assigned to one compound class in this classification scheme. The only exceptions to this are propane, methanol, and benzene, which are split between the C4-C5 alkanes and nonreactive classes. Also included in the table are estimates of the uncertainty in the assignments. The uncertainty is expressed on a scale of 0 to 4, where 0 indicates that the species is treated explicitly in the mechanism, and 4 indicates that

TABLE 4-1

NMOC CLASSES FOR THE OZIPM MECHANISM

Compound Class	Symbol	Molecular Weight	No. of Carbons Per Molecule
Ethene	ETHE	28.	2
Terminal Alkenes	PRPE	42.	3
Internal Alkenes	TBUT	56.	4
C4-C5 Alkanes	ALK4	65.	4.5
C6+ Alkanes	ALK7	100.	7
Mono-Alkylbenzenes	TOLU	92.	7
Di-Alkylbenzenes	XYLE	106.	8
Tri-Alkylbenzenes	TMBZ	120.	9
Formaldehyde	HCHO	30.	1
Acetaldehyde	ALD2	46.	2
Higher Aldehydes	RCHO	58.	3
Ketones	MEK	72.	4
Nonreactive	NROG	15.	1

TABLE 4-2

NMOC CLASSES FOR THE CONDENSED MECHANISM

Compound Class	Symbol	Molecular Weight	No. of Carbons Per Molecule
Ethene	ETHE	28.	2
Higher Alkenes	ALKE	47.6*	3.4*
C4+ Alkanes	ALKA	84.9*	5.92*
Mono-Alkylbenzenes	TOLU	92.	7
Higher Aromatics	AROM	111.6*	8.4*
Formaldehyde	HCHO	30.	1
Higher Aldehydes	ALD2	46.	2
Ketones	MEK	72.	4
Nonreactive	NROG	15.	1

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*Default values. Speciated emission inventory data should be used, if available, to determine more accurate values.

TABLE 4-3

ORGANIC SPECIES CLASSIFICATION FOR THE OZIPM CHEMICAL MECHANISM

ID No.	Compound Name	Classification	Uncertainty Classification
43814	1,1,1-TRICHLOROETHANE	NONREACTIVE	1
43820	1,1,2-TRICHLOROETHANE	NONREACTIVE	1
43813	1,1-DICHLOROETHANE	NONREACTIVE	1
45225	1,2,3-TRIMETHYLBENZENE	TRI-ALKYL BENZENE	1
45208	1,2,4-TRIMETHYLBENZENE	TRI-ALKYL BENZENE	1
99016	1,2-DICHLOROPROPANE	NONREACTIVE	1
45207	1,3,5-TRIMETHYLBENZENE	TRI-ALKYL BENZENE	0
43218	1,3-BUTADIENE	INTERNAL ALKENES	2
46201	1,4-DIOXANE	C6+ ALKANES	2
43213	1-BUTENE	TERMINAL ALKENES	1
98104	1-CHLOROBUTANE	C4-C5 ALKANES	2
43268	1-DECENE	TERMINAL ALKENES	3
98111	1-ETHOXY-2-PROPANOL	C6+ ALKANES	2
98113	1-HEPTANOL	C6+ ALKANES	1
98005	1-HEPTENE	TERMINAL ALKENES	3
43245	1-HEXENE	TERMINAL ALKENES	3
98037	1-METHYLCYCLOHEXANE	C6+ ALKANES	1
43267	1-NONENE	TERMINAL ALKENES	3
99901	1-OCTENE	TERMINAL ALKENES	3
43224	1-PENTENE	TERMINAL ALKENES	2
43312	1-T-2-O-4-TM-CYCLOPENTANE	C6+ ALKANES	1
43269	1-UNDECENE	TERMINAL ALKENES	3
43296	2,2,3-TRIMETHYLPENTANE	C6+ ALKANES	1
43276	2,2,4-TRIMETHYLPENTANE	C6+ ALKANES	1
43299	2,2,5-TRIMETHYLPENTANE	C6+ ALKANES	1
98033	2,2,5-TRIMETHYLHEXANE	C6+ ALKANES	1
43291	2,2-DIMETHYBUTANE	C6+ ALKANES	1
43280	2,3,3-TRIMETHYLPENTANE	C6+ ALKANES	1
43279	2,3,4-TRIMETHYLPENTANE	C6+ ALKANES	1
43234	2,3-DIMETHYL-1-BUTENE	TERMINAL ALKENES	2
98001	2,3-DIMETHYLBUTANE	C6+ ALKANES	1
43274	2,3-DIMETHYLPENTANE	C6+ ALKANES	1
98054	2,4,4-TRIMETHYL-1-PENTENE	TERMINAL ALKENES	3
98055	2,4,4-TRIMETHYL-2-PENTENE	INTERNAL ALKENES	3
43277	2,4-DIMETHYLHEXANE	C6+ ALKANES	1
43271	2,4-DIMETHYLPENTANE	C6+ ALKANES	1
43278	2,5-DIMETHYLHEXANE	C6+ ALKANES	1
98110	2-(-BUTOXYETHOXY)-ETHANOL	C6+ ALKANES	2
43308	2-BUTYLETHANOL	C6+ ALKANES	1
98108	2-BUTYLTETRAHYDROFURAN	C6+ ALKANES	2
98051	2-CHLOROTOLUENE	MONO-ALKYL BENZENE	2
43452	2-ETHOXYETHYL ACETATE	C6+ ALKANES	3
43311	2-ETHOXYETHANOL	C6+ ALKANES	2
98002	2-ETHYL-1-BUTENE	TERMINAL ALKENES	2
98112	2-ETHYL-1-HEXANOL	C6+ ALKANES	1
43310	2-METHOXYETHANOL	C6+ ALKANES	2

TABLE 4-3 (continued)

ID No.	Compound Name	Classification	Uncertainty Classification
43229	2-METHYL PENTANE	C6+ ALKANES	1
98076	2-METHYL-3-HEXANONE	KETONES	1
98004	2-METHYL-2-PENTENE	INTERNAL ALKENES	2
43228	2-METHYL-2-BUTENE	INTERNAL ALKENES	1
98040	2-METHYL-1-PENTENE	TERMINAL ALKENES	3
43225	2-METHYL-1-BUTENE	TERMINAL ALKENES	2
43275	2-METHYLHEXANE	C6+ ALKANES	1
98032	3,5,5-TRIMETHYLHEXANE	C6+ ALKANES	1
98105	3-(CHLOROMETHYL)-HEPTANE	C6+ ALKANES	2
99021	3-CARENE*	INTERNAL ALKENES	3
98041	3-HEPTENE	INTERNAL ALKENES	3
43230	3-METHYL PENTANE	C6+ ALKANES	1
43223	3-METHYL-1-BUTENE	TERMINAL ALKENES	1
43270	3-METHYL-T-2-PENTENE	INTERNAL ALKENES	2
43211	3-METHYL-1-PENTENE	TERMINAL ALKENES	2
43298	3-METHYLHEPTANE	C6+ ALKANES	1
43295	3-METHYLHEXANE	C6+ ALKANES	1
43293	4-METHYL-T-2-PENTENE	INTERNAL ALKENES	2
43297	4-METHYLHEPTANE	C6+ ALKANES	1
98042	4-NONENE	INTERNAL ALKENES	3
45221	A-METHYLSTYRENE	TERMINAL ALKENES	3
98025	A-PINENE*	INTERNAL ALKENES	3
98097	A-TERPINEOL*	INTERNAL ALKENES	3
43503	ACETALEHYDE	ACETALDEHYDE	0
43404	ACETIC ACID	NONREACTIVE	2
43551	ACETONE**	KETONES	1
43702	ACETONITRILE	NONREACTIVE	1
43206	ACETYLENE	NONREACTIVE	2
43505	ACROLEIN (ACRYLIC ALDHYDE)	ACETALDEHYDE	3
43704	ACRYLONITRILE	ETHENE	3
98085	ALKYL SUBSTITUTED CYCLOHEXANE	C6+ ALKANES	2
99001	ALLYL CHLORIDE	ETHENE	3
98015	ANTHRACENE	TRI-ALKYL BENZENE	3
98020	B-METHYLSTYRENE	INTERNAL ALKENES	3
98026	B-PINENE*	TERMINAL ALKENES	3
45201	BENZENE	NONREACTIVE 70% C6+ ALKANES 30%	3
45402	BENZOIC ACID	NONREACTIVE	3
98024	BENZYL CHLORIDE	MONO-ALKYL BENZENE	3
99017	BROMODICHLOROMETHANE	NONREACTIVE	1
99019	BROMOFORM	NONREACTIVE	1
98080	BUTANDIOL	C6+ ALKANES	2
98074	BUTYL CELLOSOLVE	C6+ ALKANES	2
43510	BUTYRALDEHYDE	HIGHER ALDEHYDES	1
98086	C2 ALKYL DECALIN	C6+ ALKANES	2
98084	C2 ALKYL INDAN	DI-ALKYL BENZENE	3
43512	C5 ALDEHYDE	HIGHER ALDEHYDES	2
98075	C5 ESTER	C4-C5 ALKANES	3
98095	C6 ALDEHYDE	HIGHER ALDEHYDES	2

TABLE 4-3 (continued)

ID No.	Compound Name	Classification	Uncertainty Classification
98093	C6 ESTER	C6+ ALKANES	3
98096	CARBITOL	C6+ ALKANES	2
98030	CARBON SULFIDE	NONREACTIVE	4
43807	CARBON TETRABROMIDE	NONREACTIVE	0
43804	CARBON TETRACHLORIDE	NONREACTIVE	0
98031	CARBONYL SULFIDE	NONREACTIVE	1
98087	CARVOMENTHENE*	INTERNAL ALKENE	3
98088	CARVONE*	INTERNAL ALKENE	3
43443	CELLOSOLVE ACETATE	C6+ ALKANES	3
99020	CHLORODIBROMOMETHANE	NONREACTIVE	1
43825	CHLORODIFLUOROMETHANE (F-22)	NONREACTIVE	1
43830	CHLOROFLUOROHYDROCARBONS	NONREACTIVE	3
43803	CHLOROFORM	NONREACTIVE	1
43827	CHLOROPENTAFLUOROETHANE (F-115)	NONREACTIVE	0
43826	CHLOROTRIFLUOROMETHANE (F-13)	NONREACTIVE	0
43217	CIS-2-BUTENE	INTERNAL ALKENES	1
43227	CIS-2-PENTENE	INTERNAL ALKENES	1
43227	CIS-3-PENTENE	INTERNAL ALKENES	1
98019	CRYOFLOURANE (F 114)	NONREACTIVE	1
43264	CYCLOHEXANONE	KETONES	2
43248	CYCLOHEXANE	C6+ ALKANES	1
43273	CYCLOHEXENE	INTERNAL ALKENES	2
43292	CYCLOPENTENE	INTERNAL ALKENES	2
43242	CYCLOPENTANE	C4-C5 ALKANES	1
43207	CYCLOPROPANE	NONREACTIVE	1
98027	D-LIMONENE*	INTERNAL ALKENES	3
43320	DIACETONE ALCOHOL	HIGHER KETONE	3
99015	DIBENZOFURAN	DI-ALKYL BENZENE	3
98107	DIBUTYL ETHER	C6+ ALKANES	1
43823	DICHLORODIFLUOROMETHANE (F-12)	NONREACTIVE	0
43802	DICHLOROMETHANE	NONREACTIVE	1
43828	DICHLOROTETRAFLUOROETHANE	NONREACTIVE	0
98062	DIETHYLCYCLOHEXANE	C6+ ALKANES	1
43450	DIMETHYL FORMAMIDE	DI-ALKYL BENZENE	4
98018	DIMETHYL ETHER	C4-C5 ALKANES	1
98059	DIMETHYLCYCLOHEXANE	C6+ ALKANES	1
45103	DIMETHYLETHYLBENZENE	TRI-ALKYL BENZENE	1
98091	DIMETHYLHEPTANE	C6+ ALKANES	1
98012	DIMETHYLNAPHTHALENE	TRI-ALKYL BENZENE	3
98017	DM-2,3,DH-1H-INDENE	TRI-ALKYL BENZENE	3
99006	EPICHLOROHYDRIN	NONREACTIVE	2
43202	ETHANE	NONREACTIVE	2
43433	ETHYL ACETATE	C4-C5 ALKANES	3
43438	ETHYL ACRYLATE	TERMINAL ALKENE	3
43302	ETHYL ALCOHOL	C4-C5 ALKANES	1
43812	ETHYL CHLORIDE	NONREACTIVE	1
43351	ETHYL ETHER	C4-C5 ALKANES	1
98106	ETHYL ISOPROPYL ETHER	C6+ ALKANES	1
43219	ETHYLACETYLENE	ETHENE	3

TABLE 4-3 (continued)

ID No.	Compound Name	Classification	Uncertainty Classification
43721	ETHYLAMINE	DI-ALKYL BENZENE	4
45203	ETHYLBENZENE	MONO-ALKYL BENZENE	1
43288	ETHYLCYCLOHEXANE	C6+ ALKANES	1
98057	ETHYLCYCLOPENTANE	C6+ ALKANES	1
99014	ETHYLENE DIBROMIDE	NONREACTIVE	2
43601	ETHYLENE OXIDE	NONREACTIVE	2
43815	ETHYLENE DICHLORIDE	NONREACTIVE	2
43370	ETHYLENE GLYCOL	C4-C5 ALKANES	3
43203	ETHYLENE	ETHENE	0
98011	ETHYLNAPHTHALENE	TRI-ALKYL BENZENE	3
43502	FORMALDEHYDE	FORMALDEHYDE	0
99902	FURAN	DI-ALKYL BENZENE	3
43368	GLYCOL	C4-C5 ALKANES	3
43367	GLYCOL ETHER	C6+ ALKANES	2
99903	GLYOXAL**	FORMALDEHYDE	2
43232	HEPTANE	C6+ ALKANES	1
98077	HEPTANONE	KETONES	1
99007	HEXACHLOROCYCLOPENTADIENE	NONREACTIVE	2
43231	HEXANE	C6+ ALKANES	1
43371	HEXYLENE GLYCOL	C6+ ALKANES	2
98044	INDAN	DI-ALKYL BENZENE	3
98048	INDENE	TRI-ALKYL BENZENE	3
98115	ISOAMYL ISOBUTYRATE	C6+ ALKANES	3
43214	ISOBUTANE	C4-C5 ALKANES	1
43451	ISOBUTYL ISOBUTYRATE	C6+ ALKANES	3
43446	ISOBUTYL ACETATE	C4-C5 ALKANES	3
43306	ISOBUTYL ALCOHOL	C4-C5 ALKANES	1
98047	ISOBUTYLBENZENE	MONO-ALKYL BENZENE	1
43215	ISOBUTYLENE	TERMINAL ALKENES	2
98036	ISOBUTYRALDEHYDE	HIGHER ALDEHYDES	1
99904	ISOMERS OF HEPTENE	INTERNAL ALKENES	3
43105	ISOMERS OF HEXANE	C6+ ALKANES	1
43106	ISOMERS OF HEPTANE	C6+ ALKANES	1
99905	ISOMERS OF HEXENE	INTERNAL ALKENES	3
45102	ISOMERS OF XYLENE	DI-ALKYL BENZENE	3
45105	ISOMERS OF BUTYLBENZENE	MONO-ALKYL BENZENE	3
43108	ISOMERS OF NONANE	C6+ ALKANES	1
45106	ISOMERS OF DIETHYLBENZENE	DI-ALKYL BENZENE	3
43110	ISOMERS OF UNDECANE	C6+ ALKANES	2
43122	ISOMERS OF PENTANE	C4-C5 ALKANES	1
45104	ISOMERS OF ETHYLTOLUENE	DI-ALKYL BENZENE	3
43112	ISOMERS OF DODECANE	C6+ ALKANES	2
43107	ISOMERS OF OCTANE	C6+ ALKANES	1
43109	ISOMERS OF DECANE	C6+ ALKANES	2
99906	ISOMERS OF OCTENE	INTERNAL ALKENES	3
43243	ISOPRENE*	INTERNAL ALKENES	2
98043	ISOPROPYLBENZENE (CUMENE)	MONO-ALKYL BENZENE	1
43444	ISOPROPYL ACETATE	C4-C5 ALKANES	3
43304	ISOPROPYL ALCOHOL	C4-C5 ALKANES	1

TABLE 4-3 (continued)

ID No.	Compound Name	Classification	Uncertainty Classification
98089	ISOPULEGONE*	TERMINAL ALKENES	3
98056	ISOVALERALDEHYDE	HIGHER ALDEHYDES	2
43119	LACTOL SPIRITS	C6+ ALKANES	4
98022	M-CRESOL (3-M-BENZENOL)**	MONO-ALKYL BENZENE	2
98045	M-DIETHYLBENZENE	DI-ALKYL BENZENE	1
45212	M-ETHYLTOLUENE	DI-ALKYL BENZENE	1
45205	M-XYLENE	DI-ALKYL BENZENE	0
99008	MALEIC ANHYDRIDE	NONREACTIVE	2
43201	METHANE	NONREACTIVE	1
43432	METHYL ACETATE	NONREACTIVE	2
43301	METHYL ALCOHOL	NONREACTIVE 50% C4-C5 ALKANES 50%	3
43445	METHYL AMYL ACETATE	C6+ ALKANES	3
43561	METHYL AMYL KETONE	KETONES	1
43819	METHYL BROMIDE	NONREACTIVE	1
43801	METHYL CHLORIDE	NONREACTIVE	1
43552	METHYL ETHYL KETONE	KETONES	0
98114	METHYL ISOBUTYRATE	C4-C5 ALKANES	3
43560	METHYL ISOBUTYL KETONE	KETONES	1
43559	METHYL N-BUTYL KETONE	KETONES	1
43209	METHYLACETYLENE	ETHENE	3
98016	METHYLANTHRACENE	TRI-ALKYL BENZENE	3
43262	METHYLCYCLOPENTANE	C6+ ALKANES	1
43261	METHYLCYCLOHEXANE	C6+ ALKANES	1
43272	METHYLCYCLOPENTENE	INTERNAL ALKENES	3
43805	METHYLENE BROMIDE	NONREACTIVE	0
98010	METHYLNAPHTHALENE	TRI-ALKYL BENZENE	3
45234	METHYLPROPYLBENZENE	DI-ALKYL BENZENE	1
43118	MINERAL SPIRITS	MONO-ALKYL BENZENE	4
45801	MONOCHLOROBENZENE	NONREACTIVE	3
43212	N-BUTANE	C4-C5 ALKANES	1
43305	N-BUTYL ALCOHOL	C4-C5 ALKANES	1
43435	N-BUTYL ACETATE	C4-C5 ALKANES	3
43238	N-DECANE	C6+ ALKANES	2
43255	N-DODECANE	C6+ ALKANES	2
43220	N-PENTANE	C6+ ALKANES	1
98063	N-PENTYLCYCLOHEXANE	C6+ ALKANES	2
43303	N-PROPYL ALCOHOL	C4-C5 ALKANES	1
45209	N-PROPYLBENZENE	MONO-ALKYL BENZENE	1
45101	NAPHTHA	MONO-ALKYL BENZENE	4
98046	NAPHTHALENE	TRI-ALKYL BENZENE	3
99009	NITROBENZENE	NONREACTIVE	3
43235	NONANE	C6+ ALKANES	1
98021	O-CRESOL (2-M-BENZENOL)**	MONO-ALKYL BENZENE	2
45211	O-ETHYLTOLUENE	DI-ALKYL BENZENE	1
45204	O-XYLENE	DI-ALKYL BENZENE	1
43233	OCTANE	C6+ ALKANES	1
98023	P-CRESOL (4-M-BENZENOL)**	MONO-ALKYL BENZENE	2

TABLE 4-3 (continued)

ID No.	Compound Name	Classification	Uncertainty Classification
45807	P-DICHLOROBENZENE	NONREACTIVE	3
45206	P-XYLENE	DI-ALKYL BENZENE	1
98094	PENTYL ALCOHOL	C4-C5 ALKANES	1
43817	PERCHLOROETHYLENE	NONREACTIVE	1
45300	PHENOLS**	MONO-ALKYL BENZENE	3
98028	PHTHALIC ANHYDRIDE	DI-ALKYL BENZENE	3
43208	PROPADIENE	TERMINAL ALKENES	3
43204	PROPANE	NONREACTIVE 50% C4-C5 ALKANES 50%	3
43504	PROPIONALDEHYDE	HIGHER ALDEHYDES	1
43434	PROPYL ACETATE	C4-C5 ALKANES	3
45108	PROPYLBENZENE	MONO-ALKYL BENZENE	1
98109	PROPYLCYCLOHEXANONE	KETONES	2
43602	PROPYLENE OXIDE	C4-C5 ALKANES	3
43369	PROPYLENE GLYCOL	C4-C5 ALKANES	2
43205	PROPYLENE	TERMINAL ALKENES	0
98013	PROPYLNAPHTHALENE	TRI-ALKYL BENZENE	3
45216	SEC-BUTYLBENZENE	MONO-ALKYL BENZENE	1
45220	STYRENE	TERMINAL ALKENES	3
98116	SUBSTITUTED C7 ESTER (C12)	C6+ ALKANES	3
98117	SUBSTITUTED C9 ESTER (C12)	C6+ ALKANES	3
43123	TERPENES*	INTERNAL ALKENES	3
98079	TERPINENE*	INTERNAL ALKENES	3
45215	TERT-BUTYLBENZENE	MONO-ALKYL BENZENE	1
43309	TERT-BUTYL-ALCOHOL	C4-C5 ALKANES	1
43390	TETRAHYDROFURAN	C6+ ALKANES	1
45232	TETRAMETHYLBENZENE	TRI-ALKYL BENZENE	1
45202	TOLUENE	MONO-ALKYL BENZENE	0
99018	TRANS-1,2-DICHLOROETHENE	ETHENE	3
43216	TRANS-2-BUTENE	INTERNAL ALKENES	0
43227	TRANS-2-PENTENE	INTERNAL ALKENES	1
43226	TRANS-2-PENTENE	INTERNAL ALKENES	1
43227	TRANS-3-PENTENE	INTERNAL ALKENES	1
45233	TRI/TETRAALKYL BENZENE	TRI-ALKYL BENZENE	1
43821	TRICHLOROTRIFLUOROETHANE	NONREACTIVE	0
43811	TRICHLOROFLUOROMETHANE	NONREACTIVE	0
43824	TRICHLOROETHYLENE	ETHENE	3
45107	TRIMETHYLBENZENE	TRI-ALKYL BENZENE	1
43740	TRIMETHYL AMINE	TRI-ALKYL BENZENE	4
98060	TRIMETHYLCYCLOHEXANE	C6+ ALKANES	1
98058	TRIMETHYLCYCLOPENTANE	C6+ ALKANES	1
98014	TRIMETHYLNAPHTHALENE	TRI-ALKYL BENZENE	3
43822	TRIMETHYLFLUOROSILANE	NONREACTIVE	1
43241	UNDECANE	C6+ ALKANES	2
43860	VINYL CHLORIDE	ETHENE	3
45401	XYLENE BASE ACIDS	DI-ALKYL BENZENE	4

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*Biogenic compound.

**These species can either be represented by the assigned class or explicitly.

TABLE 4-3 (continued)

Uncertainty Classifications:

0 = Explicitly represented in mechanism (for reactive compounds), or known not to react in the troposphere (for nonreactive compounds)

1 = Representation shown is probably a good approximation

2 = Representation shown may not be a good approximation, but the mechanism does not contain more appropriate species.

3 = Representation shown is probably a poor approximation, but the mechanism does not contain more appropriate species.

4 = Appropriate representation is unknown.

reactivity is totally unknown. Examples of the uncertainty classification are described in Table 4-4.

Chemical structure is largely the basis for the assignment of the individual species to classes. Alkanes are assigned to one of the alkane classes on the basis of carbon number. Alkenes are assigned based on the position of the double bond within the molecule (i.e., on whether the double bond is located in the terminal position or in an internal position). The aromatics are assigned based on the number of alkyl groups attached to the benzene ring. Aldehydes are assigned on the basis of carbon number. However, about 20% of the compounds on the list are not kinetically or structurally similar to any of the surrogate species. These are the species that have been assigned a high uncertainty rating (3 or 4) in Table 4-3. The assignments for these species are primarily based on similarity between their OH rate constants (when available) and the OH rate constants of the surrogate species in the mechanism and, secondarily, on similarity of structure and reactivity of products (when known). The OH rate constants were obtained from Atkinson (1986). Although these compounds represent 20% of the species on the list, it is unlikely that they represent a significant (i.e., more than 5%) fraction of NMOC in urban areas.

Another difficulty is in the classification of the less reactive compounds. It is difficult to objectively separate the nonreactive and reactive compounds. This problem has been recognized for many years and still does not have an adequate solution because reactivity is a very complex issue. It is well established that the reactivity of organic compounds depends markedly on the NMOC/NO_x ratio of the mixture (Atkinson et al. 1983). This dependence makes it difficult to assess reactivity in absolute terms. With full recognition of their shortcomings, OH rate constants have been used as the basis for separating the nonreactive and reactive compounds in this assessment. Nonphotolyzing species with OH rate constants less than 1.E-12 molecules per cc-sec have been largely classified as nonreactive. Although the OH rate constant can be a misleading surrogate for reactivity [because the products of the reaction may or may not be reactive (Atkinson et al. 1983)], it is the only available measure of reactivity for most of the less reactive species. The cut-off of 1.E-12 molecules per cc-sec for the OH rate constant is

TABLE 4-4

EXAMPLES OF UNCERTAINTY CLASSIFICATIONS

CLASS 1:	-All alkanes, including simple alcohols or ethers, lumped with the 2 alkane classes -C3-C4 1-alkenes as terminal alkenes (propene) -C4-C5 internal alkenes as internal alkenes (2-butene) -alkylbenzenes
CLASS 2:	-Bifunctional alcohols or ethers as alkanes -Unsymmetrical disubstituted alkenes as terminal alkenes, which are represented by propene -C5 1-alkenes as terminal alkenes (propene) -C6 internal alkenes as internal alkene (2-butene) -Aromatics containing Cl's on side groups -External dialkenes as terminal alkenes -C10+ alkanes as C6+ alkanes
CLASS 3:	-Esters and other carbonyl compounds as alkanes -C6-C9 1-alkenes as terminal alkenes -C7+ internal alkenes as internal alkenes -Groups of compounds with varying classification, depending on which, where most are expected to be as classified, with uncertainty of 2 or better -C10+ 1 alkenes as terminal alkenes -Styrenes as alkenes -Naphthalenes, tetralins, or indans as di- or tri-alkyl benzenes -Furans as aromatics
CLASS 4:	-Amines as aromatics (too reactive to be classified as alkanes, but chemistry not aromatic.) -CS2 (unknown whether it promotes ozone formation)

arbitrary, but probably adequate for most urban situations where there is an abundance of more reactive compounds.

4.2 Speciation of NMOC Emissions and Ambient Data

Historically, even though the role of organics in ozone formation has been recognized for over 20 years, speciated NMOC data have not been collected on a routine basis in urban areas. Mostly because of the expense and complexity of the gas chromatographic (GC) measurement technique, speciated NMOC has only been collected for short periods, usually during special air quality studies. Similarly, direct measurements of the speciation of NMOC emissions have not been performed on a routine basis. The routine measurements have primarily quantified total VOC and NMOC.

Because there are over 300 gaseous organic species in ambient air (Hampton et al. 1982; Stump and Dropkin 1985), and the concentrations of many species are very low, researchers have had a difficult time trying to provide complete speciation of the organics. In typical applications of the GC technique, 75% to 90% of the organic carbon can be speciated; 10% to 25% cannot be identified. Some improvement on these percentages can be achieved with the scrubbing technique of Lonneman (1986), which provides a means to classify most of the otherwise unidentified compounds by carbon number and class (alkene, alkane, and aromatics). Also, the normal combination of GC and flame ionization detection (FID) methods does not detect oxygenated species such as aldehydes and ketones. Although the sum of the oxygenated species concentrations rarely exceeds 10% of the NMOC, the concentrations play a very important role as photoinitiators in the atmospheric chemistry, and knowledge of their emissions and ambient concentrations is important. Reliable techniques for measuring the oxygenated species concentrations at ambient levels have only recently become available. These techniques have not been applied widely so there is a shortage of good data for oxygenated species and an even greater shortage of side-by-side oxygenated and nonoxygenated species data.

Notwithstanding the shortcomings of the available data bases, there are data bases for speciation of NMOC emissions and ambient concentrations. Emission speciation profiles are available for a moderate number of stationary and mobile sources in the "Volatile Organic Compound Species Data Manual" (EPA 1980) and "Improvements of the Emission Inventory for ROG and NO_x in the SoCAB" (Oliver and Peoples 1985). Profiles for stationary sources are generally assigned on the basis of Source Classification Code (SCC). The detailed profiles can be transformed to NMOC class profiles using the assignments shown in Table 4-3. However, in order to speciate an entire emissions inventory, the available profiles must be extrapolated to source types that may not be very similar to the source for which the data were obtained. High-quality speciation data for mobile sources are available from EPA's "Forty-Six Car Study" (Sigsby et al. 1987).

Speciated ambient NMOC data are needed for photochemical modeling. It is recommended that area-specific data be employed in the modeling whenever possible. Recognizing that speciated NMOC ambient data are often not available, an analysis of recent 6:00 to 9:00 a.m. NMHC data from urban areas was performed. The data selected for analysis were 500 samples collected by EPA in 29 urban areas during 1984 and 1985 (Lonneman 1986). These data were collected and analyzed with a consistent methodology and have an unusually small percentage of unidentified carbon. However, many of the higher molecular weight compounds were only identified by carbon number and by class (alkane, alkene, or aromatic), so the actual splits between the two types of the higher alkenes and two types of higher aromatics are uncertain. The average normalized NMHC composition of the data from each city was computed. A grand average profile was determined from the average profile in each city. Data from four cities along the Gulf Coast were not included in the grand average because their average composition profiles showed anomalously high alkene fractions and low aromatic fractions. The results of the analysis are shown in Table 4-5. The data indicate that the NMHC detected by GC are 49% C4+ alkanes, 13% alkenes, 26% aromatics, and 12% nonreactive.

Ambient data for oxygenated species were reviewed in order to establish default composition fraction. Most of the available data has been collected in the Los Angeles Basin. Data reported by Grosjean (1982), Grosjean and Lloyd (1982), and Grosjean and Fung (1984) were examined. Figure 4-1 shows frequency distributions of the concentrations

TABLE 4-5

URBAN NMHC COMPOSITION DETERMINED FROM DATA COLLECTED BY LONNEMAN IN 1984 AND 1985 (Carbon Fractions)

Location	C4-C5 Alkanes	C6+ Alkanes	Ethene	Terminal Alkenes	Internal Alkenes	Mono-alkyl Benzenes	Di-alkyl Benzenes	Tri-alkyl Benzenes	Unreactive	No. of Samples
Akron, OH	.203	.261	.031	.030	.055	.147	.039	.050	.184	10
Atlanta, GA	.166	.337	.038	.050	.046	.185	.038	.052	.087	7
Baton Rouge, LA	.243	.254	.033	.071	.033	.117	.038	.031	.180	14
Birmingham, AL*	.113	.459	.030	.033	.034	.132	.044	.058	.098	6
Boston, MA	.262	.228	.029	.067	.047	.198	.027	.045	.096	8
Charlotte, NC	.188	.296	.045	.054	.044	.179	.045	.052	.097	16
Chattanooga, TN*	.114	.322	.020	.081	.080	.189	.065	.067	.061	12
Cincinnati,OH	.258	.270	.015	.046	.047	.123	.080	.114	.047	7
Cleveland, OH	.243	.220	.036	.041	.039	.167	.052	.045	.155	17
Dallas, TX	.204	.288	.031	.047	.041	.177	.040	.051	.122	34
El Paso, TX	.245	.265	.036	.047	.050	.150	.031	.040	.137	27
Fort Worth, TX	.213	.283	.038	.046	.047	.155	.035	.041	.143	32
Houston, TX	.251	.205	.030	.088	.053	.114	.055	.028	.176	21
Indianapolis, IN	.219	.281	.042	.041	.034	.168	.040	.055	.121	10
Kansas City, MO	.207	.328	.032	.040	.039	.161	.030	.043	.120	29
Lake Charles, LA	.256	.192	.023	.045	.026	.099	.053	.034	.274	15
Memphis, TN	.164	.330	.027	.035	.042	.221	.057	.063	.060	8
Miami, FL	.216	.294	.033	.035	.034	.188	.041	.063	.095	3
Philadelphia, PA	.222	.233	.046	.155	.040	.199	.049	.040	.122	31
Portland, ME	.281	.209	.022	.071	.049	.127	.105	.100	.100	14
Richmond, VA	.173	.291	.032	.047	.049	.197	.041	.078	.094	24
St. Louis, MO	.198	.256	.028	.050	.038	.187	.051	.049	.142	17
Washington, DC	.213	.275	.041	.055	.050	.181	.039	.060	.087	21
West Palm Beach, FL*	.138	.462	.026	.031	.039	.137	.040	.059	.067	8
Wilkes-Barre, PA	.203	.286	.058	.045	.039	.146	.039	.048	.136	10
Average	.208	.285	.033	.054	.044	.162	.047	.052	.120	401
Standard Deviation**	.044	.064	.009	.025	.010	.031	.016	.017	.048	

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*There are possible problems with these data, as indicated by the low C4-C5 alkane fraction.

**Standard deviation of the average profiles for each city.

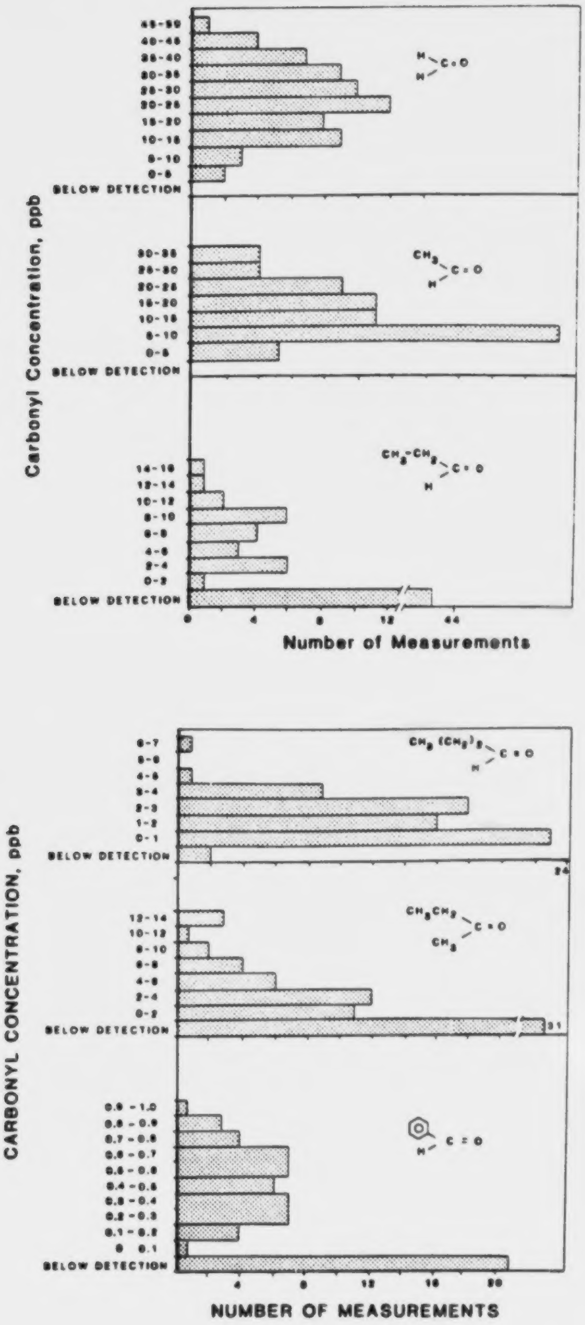

Figure 4-1. Frequency distribution of carbonyl concentrations observed in Claremont, California (from Grosjean 1982).

of individual carbonyls observed in Claremont, California (east of Los Angeles), by Grosjean (1982). Formaldehyde, acetaldehyde, propanol, butanol, MEK, and benzaldehyde concentrations are shown. These data indicate that formaldehyde and acetaldehyde account for more than 70% of the carbonyls on a carbon basis. They also indicate that formaldehyde concentrations generally exceed acetaldehyde concentrations (on a carbon basis). Figure 4-2 shows a plot of the morning total aldehyde concentrations versus NMOC concentrations measured by GC in Los Angeles (Grosjean and Lloyd 1982). The data show a lot of scatter. The line labeled "STANDARD EKMA" on the figure is the 5% aldehydes line. While most of the aldehyde concentrations are less than 5% of the NMOC, some points are slightly above the line. Although the data do not indicate a clear relationship between aldehydes and NMOC detected by GC/FID, the data are also not inconsistent with the 5% aldehyde assumption historically employed in OZIPP/EKMA. The 5% aldehyde assumption appears to be a fairly realistic upper limit assumption and is recommended for use in the absence of better data.

Additional ambient NMOC data collected by aircraft were analyzed to provide default upper boundary condition information for modeling. The most comprehensive data set for speciated NMOC above the morning mixing height (aloft) is that collected and analyzed by Washington State University in the summer of 1985 (WSU 1986). The flight plans were designed to capture the NMOC aloft at locations slightly upwind of four cities: Atlanta, Birmingham, Dallas, and Tulsa. Although these samples do not have nearly as many species identified as those analyzed by Lonneman (1986), they do include formaldehyde and acetaldehyde. The average normalized NMOC composition aloft and upwind of each city is shown in Table 4-6. Also shown are the average NMOC concentrations calculated from all samples and from the samples used to determine the average speciation profiles. Only those profiles with total NMOC concentrations exceeding 15 ppbC were used for determining the speciation. Profiles with less than 15 ppbC of NMOC were considered unreliable for speciation because of potential detection problems at low concentrations. The data show the NMOC consist of 25% C4+ alkanes, 4% alkenes, 8% aromatics, 7% aldehydes, 33% unreactive, and 23% unidentified. The unidentified species are probably long-chain alkanes

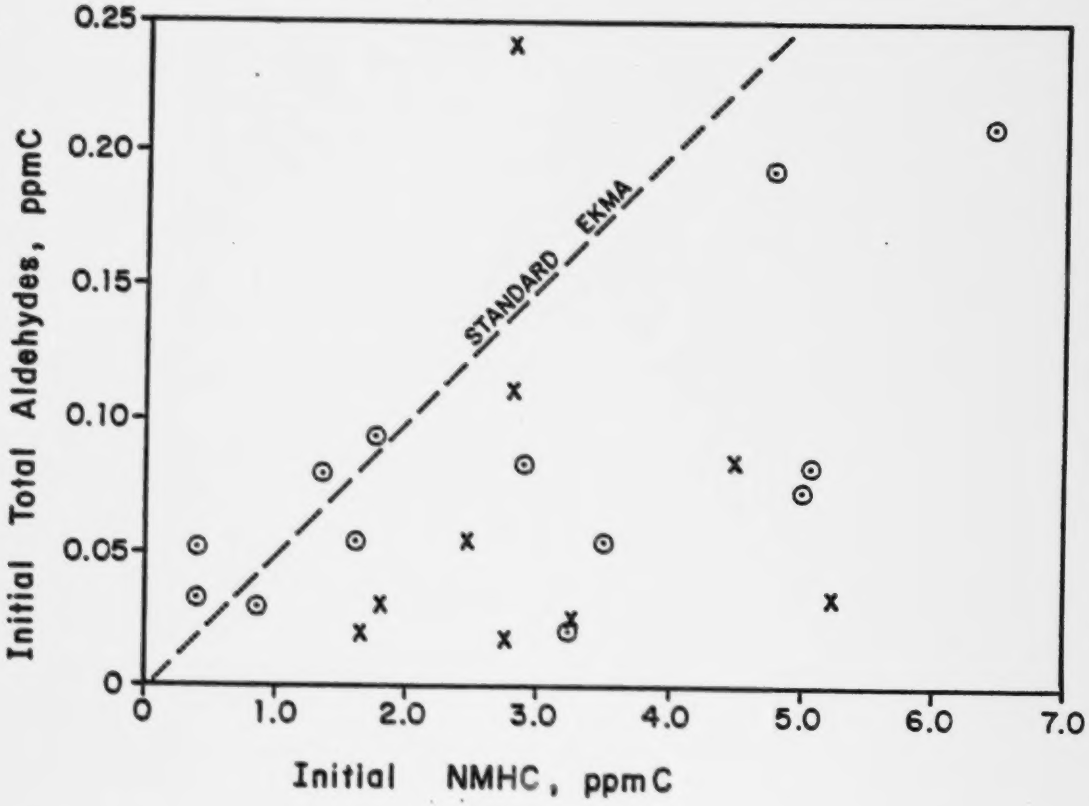

Figure 4-2. Initial aldehyde concentration versus initial NMHC for captive air experiments. 0 = valid data points, x = potentially low aldehyde concentration due to high blank correction. Standard EKMA assumes aldehydes are 5% of NMHC levels.

TABLE 4-6

NMOC COMPOSITION AND CONCENTRATIONS ALOFT*

Compound Class	Atlanta	Birmingham	Dallas	Tulsa	Average
	Carbon Fraction of NMOC**				
C4-C5 Alkanes	.211	.211	.153	.247	.212
C6+ Alkanes	.027	.023	.033	.044	.035
Ethene	.007	.014	.004	.019	.012
Terminal Alkenes	.036	.012	.013	.022	.023
Internal Alkenes	-	-	-	-	-
Mono-alkylbenzenes	.126	.032	.037	.016	.056
Di-alylbenzenes	.020	.019	.022	.015	.018
Tri-alkylbenzenes	-	-	-	-	-
Unreactive	.308	.306	.272	.405	.337
Formaldehyde	.024	.018	.053	.084	.054
Acetaldehyde	.019	.011	.012	.023	.018
Unidentified	.222	.353	.402	.124	.235
	Total NMOC Concentrations (ppbC)				
NMOC - all samples	35.0	20.6	41.3	52.7	37.4
NMOC - composition samples	46.4	40.1	48.2	56.4	47.8

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*Determined from Washington State University Aircraft observations made in 1985.

**NMOC is expressed in ppbC and includes carbonyls.

and aromatics (Grosjean and Lloyd 1982). The average NMOC concentration was 37 ppbC based on all samples and 48 ppbC based on the samples used for developing the speciation profiles.

The final recommended speciation profiles for NMOC in the surface layer and above the mixed layer in urban areas are shown in Table 4-7. The profile fractions were rounded off and slightly altered based on our judgement. Note that fractions for the higher aldehyde and ketone classes have been omitted. Since the data for these species are so sparse, their fractions have been assumed to be zero. Actually, part of the carbon assigned to acetaldehyde could be assigned to these classes (perhaps 0.5% NMOC each); however, this is not likely to have much effect on predictions. Lastly, plausible ranges of the speciation fractions are shown in Table 4-8. The ranges generally reflected ±50% variations about the mean fractions. If ambient samples show variations beyond these ranges (particularly the upper values), then the sample may reflect strong influence by local point sources and may not be representative of the entire urban area.

TABLE 4-7

RECOMMENDED DEFAULT NMOC COMPOSITION PROFILES

Compound Class	Carbon Fractions of NMOC Surface Layer	 Aloft
C4-C5 Alkanes	.21	.21
C6+ Alkanes	.28	.18
Ethene	.03	.015
Terminal Alkenes	.06	.03
Internal Alkenes	.04	.005
Mono-alkylbenzenes	.16	.07
Di-alylbenzenes	.06	.04
Tri-alkylbenzenes	.04	.02
Formaldehyde	.03	.05
Acetaldehyde	.02	.03
Unreactive	.07	.35

TABLE 4-8

RANGE OF NMOC COMPOSITION FRACTIONS

Compound Class	Carbon Fractions of NMOC Surface Layer	 Aloft
C4-C5 Alkanes	.11 - .31	.11 - .31
C6+ Alkanes	.14 - .42	.09 - .27
Ethene	.015 - .045	.0 - .03
Terminal Alkenes	.03 - .09	.0 - .045
Internal Alkenes	.02 - .06	.0 - .01
Mono-alkylbenzenes	.08 - .24	.04 - .11
Di-alylbenzenes	.03 - .09	.0 - .06
Tri-alkylbenzenes	.02 - .06	.0 - .04
Formaldehyde	.015 - .06	.01 - .08
Acetaldehyde	.01 - .04	.01 - .08
Unreactive	.04 - .11	.15 - .75

5. SENSITIVITY ANALYSIS

Sensitivity analysis was performed with the updated mechanism to identify the important input parameters in typical urban applications of photochemical AQS models. The sensitivity analysis was carried out using Version 3 of the OZIPM model (Hogo and Whitten 1986) with the mechanism shown in Table 3-4. The OZIPM model is a fairly versatile photochemical box model that is designed for use with the Empirical Kinetic Modeling Approach (EKMA) (Gibson et al. 1981; EPA 1984). It was selected for this analysis because EPA expects the OZIPM model (with this or other mechanisms) to be used extensively for control strategy evaluations in the next set of State Implementation Plans.

Unlike other photochemical model sensitivity studies that examine relationships between input parameters and maximum ozone concentrations (e.g., see Seigneur et al. 1981), this analysis examines the relationships between the input parameters and the NMOC control requirement needed to achieve compliance with the National Ambient Air Quality Standard (NAAQS) for ozone. The NMOC control requirement determined from an EKMA analysis was selected as the output parameter because it is, in fact, the parameter that is most important to air quality planners. Fortunately, the version of the OZIPM model used in the analysis calculates the NMOC control requirement directly so the uncertainty associated with the graphical approach required with earlier versions is avoided.

5.1 Baseline Conditions and Parameter Variations

The matrix of runs for the sensitivity analysis was designed to span the plausible range of conditions in urban areas. Plausible baseline conditions and parameter variations were selected based on our experience and that of others (Jeffries et al. 1981; Shafer and Seinfeld 1985). Recognizing that the sensitivity of the model to certain parameter variations depends on the air quality and meteorology, conditions representing a range of initial NMOC/NO_x ratios and dilution rates were selected for the baseline runs. Nine baseline runs were established that represent the combinations of three initial NMOC/NO_x ratios (6, 10, and 20 ppmC/ppm) and three overall dilution factors (2, 4, and 6 times the initial volume). Model sensitivity to other parameter variations was then examined under all of these conditions.

The OZIPM model inputs for the baseline runs are summarized in Table 5-1. The solar radiation levels were calculated for the Los Angeles summer solstice at 34° latitude. The simulations were carried out from 8 a.m. to 6 p.m. Pacific daylight time, and an ambient temperature of 30°C was assumed. An initial mixing height of 250 meters was used for all of the calculations. Final mixing heights of 500, 1,000, and 1,500 meters were selected to represent low, moderate, and high dilution rate conditions. As the mixing height rises, pollutants initially above the mixed layer are entrained into the mixed layer. The baseline calculations were made using ozone and NMOC concentrations of 80 ppb and 50 ppbC, respectively, above the mixed layer. Initial concentrations of carbon monoxide, water vapor, and nitrous acid in the surface layer were set at 1, 20,000, and 0.0005 ppm, respectively. A present-day maximum ozone concentration of 0.24 ppm was assumed. Thus, the calculated NMOC control requirements are those required to reduce the maximum ozone concentration by 50% (to 0.12 ppm) assuming no change in the NO_x emissions. The initial NMOC and NO_x concentrations and emissions needed to produce the present-day maximum ozone value are determined iteratively by the model. The initial NMOC/NO_x ratio and relationship between the hourly post-8 a.m. emissions and the initial NMOC and NO_x concentrations are input to the model.

Initial NMOC/NO_x ratios of 6, 10, and 20 were used in the simulations. Emissions equivalent to 15% and 25% of the initial NMOC and NO_x, respectively, were employed for the first two hours. Emissions equivalent to 10% and 17% of the initial NMOC and NO_x, respectively, were employed for the third through fifth hours. Zero emissions were assumed after the fifth hour. It is important to note that the NMOC/NO_x ratio of the emissions was assumed to be 40% lower than the ratio in the initial concentrations. The difference in ratios reflects the common discrepancy between the observed ambient NMOC/NO_x ratios and NMOC/NO_x ratios based on estimated emission inventories (Haney and Seigneur 1985). Lastly, the recommended default NMOC composition profiles shown in Table 4-7 were employed in the baseline calculations.

TABLE 5-1

OZIPM SENSITIVITY ANALYSIS - BASELINE CASE INPUTS

Place:	Los Angeles, CA
Lattitude:	34. degrees
Longitude:	118. degrees
Time Zone:	8.
Date:	June 21, 1986
Initial Mixing Height:	250 m at 0800
Final Mixing Height(s):	500 m at 1400 hours 1000m at 1400 hours 1500m at 1400 hours
Temperature:	30°C
Ozone aloft:	0.08 ppm
NMOC aloft:	0.05 ppmC
Initial Values: (Surface layer)	[CO] = 1 ppm [HONO] = 0.5 ppb [H2O] = 20,000 ppm
Present Day Ozone:	0.24 ppm
Future NOx:	Same as present day
NMOC/NOx Ratio(s):	6 ppmC/ppm 10 ppmC/ppm 20 ppmC/ppm

Emission Fractions of Initial Values:

Hour	NMOC	NO_x
8	.15	.25
9	.15	.25
10	.10	.17
11	.10	.17
12	.10	.17

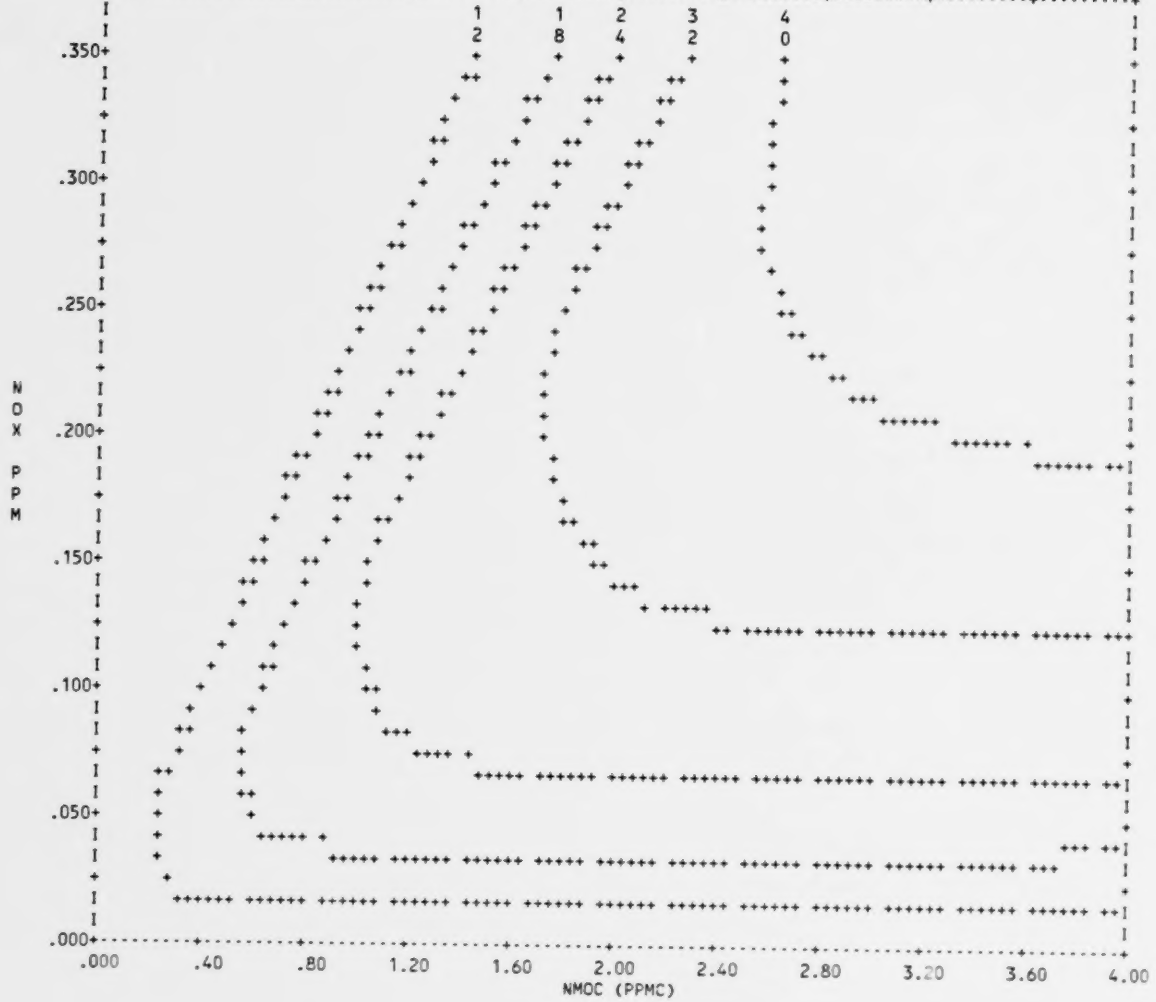
NMOC Composition: Default Profiles

The ozone isopleth diagram for baseline conditions with a 1,000-meter final mixing height is shown in Figure 5-1. This figure shows that the shape of the isopleth diagram generated with the updated chemical mechanism is very similar to the shape of previously-reported diagrams (Gibson et al. 1981).

The input parameter variations for the sensitivity analysis are summarized in Tables 5-2 and 5-3. A significant number of the runs involved variations in the NMOC composition and NMOC concentration aloft because previous studies indicated that these are important input parameters (Seigneur et al. 1981; Shafer and Seinfeld 1985). Four variations in the NMOC composition in the surface layer were investigated. The profiles, shown in Table 5-3, represent high and low reactivity mixtures of the nonoxygenated species and high and low aldehyde content mixtures for the oxygenated species. The high and low reactivity profiles were constructed by increasing and decreasing the fractions of the more reactive nonoxygenated compounds, i.e., alkenes, di-alkylbenzenes, and tri-alkylbenzenes, by 50%. The fractions of the less reactive compounds, i.e., the alkanes and mono-alkylbenzenes, were adjusted by ~18% to account for 50% changes in the more reactive compounds fractions. The nonreactive fraction was not changed in these profiles. However, in the high and low aldehyde profiles where the total aldehyde content was changed to represent 10% and 1% of the total carbon, respectively, the nonreactive fractions were adjusted to account for the changes in aldehyde content.

Seven combinations of NMOC concentrations and composition aloft were investigated. Concentrations of 10 and 150 ppbC were used to span the plausible range of NMOC concentrations aloft. An additional run with 40 ppbC, instead of 50 ppbC, aloft was made to more closely reflect the average level observed in the 1985 Washington State University aircraft study. High-reactivity, low-reactivity, and high-aldehyde composition profiles were constructed for NMOC aloft using the same approach as used for the variations in surface layer reactivity (i.e., ±50% variation in the fractions of the more reactive species).

Additional sensitivity runs were designed to investigate the importance of reductions in ozone aloft, future NO_x emissions, and post-8 a.m. emissions. Separate runs were carried out assuming zero



THE O3 LINES ARE .12 .18 .24 .32 AND .40 PPM

FIGURE 5-1. OZONE ISOPLETH DIAGRAM FOR BASELINE CONDITONS WITH SAPRC/ERT MECHANISM

TABLE 5-2

PARAMETER VARIATIONS IN THE OZIPM SENSITIVITY ANALYSIS

NMOC/NOx Ratios:	6, 10, and 20
Max. Mixing Heights:	500, 1000, and 1500 m
Surface Layer NMOC Composition:	Low reactivity High reactivity Low aldehydes High aldehydes
NMOC Aloft:	10 ppbC - baseline reactivity 40 ppbC - baseline reactivity 150 ppbC - baseline reactivity 50 ppbC - high aldehydes 50 ppbC - low reactivity 50 ppbC - high reactivity 150 ppbC - high reactivity
Ozone Aloft:	Zero
Future NOx:	30% reduction
Post 8 AM Emissions:	Zero
Present Day Ozone:	0.18 & 0.40 ppm
Initial Values: (Surface Layer)	[PAN] = 5 ppb [HONO] = 4 ppb [HONO] = 0 ppb
Photolysis Rates:	20% reduction in all rates 20% reduction in NO2 rate 20% reduction in HCHO rates

TABLE 5-3

NMOC COMPOSITION PROFILES USED IN THE OZIPM SENSITIVITY ANALYSIS

SURFACE LAYER NMOC COMPOSITION PROFILES

	Carbon Fractions of NMOC			
Compound Class	Low Reactivity	High Reactivity	Low Aldehydes	High Aldehydes
C4-C5 Alkanes	.247	.173	.21	.21
C6+ Alkanes	.33	.23	.28	.28
Ethene	.015	.045	.03	.03
Terminal Alkenes	.03	.09	.06	.06
Internal Alkenes	.02	.06	.04	.04
Mono-alkylbenzenes	.188	.132	.16	.16
Di-alylbenzenes	.03	.09	.06	.06
Tri-alkylbenzenes	.02	.06	.04	.04
Formaldehyde	.03	.03	.006	.06
Acetaldehyde	.02	.02	.004	.04
Unreactive	.07	.07	.11	.02

NMOC ALOFT COMPOSITION PROFILES

	Carbon Fractions of NMOC		
Compound Class	Low Reactivity	High Reactivity	High Aldehydes
C4-C5 Alkanes	.235	.185	.21
C6+ Alkanes	.202	.158	.18
Ethene	.0075	.0225	.015
Terminal Alkenes	.015	.045	.03
Internal Alkenes	.0025	.0075	.005
Mono-alkylbenzenes	.078	.062	.07
Di-alylbenzenes	.02	.06	.04
Tri-alkylbenzenes	.01	.03	.02
Formaldehyde	.05	.05	.10
Acetaldehyde	.03	.03	.06
Unreactive	.35	.35	.27

concentration of ozone aloft, 30% reduction in future NO_x emissions, and without post-8 a.m. emissions. Simulations were also carried out to examine the sensitivity of the NMOC control requirement to the present-day maximum ozone concentrations. Ozone concentrations of 0.18 and 0.40 ppm were employed for this purpose. All of these parameter variations were investigated at three $NMOC/NO_x$ ratios and three dilution factors.

Additional investigations of the sensitivity to initial values of PAN and nitrous acid and photolysis rates were performed at three $NMOC/NO_x$ ratios and just one dilution factor. Separate simulations were carried out with initial PAN concentrations of 5 ppb and initial HONO concentrations of 0 and 4 ppb. The photolysis rate sensitivity runs included ones with 20% reduction in all photolytic rates, 20% reduction in only the NO_2 photolysis rate, and 20% reduction in only the formaldehyde photolysis rates from their clear sky values.

5.2 Sensitivity Analysis Results

The predicted NMOC control requirements calculated in the baseline runs and in the parameter variation runs are shown in Table 5-4. The relative change in the control requirements from the corresponding baseline results are shown in Table 5-5. The baseline runs predict control requirements of 29%, 58%, and 80% for the 1,000-meter final mixing height cases with initial $NMOC/NO_x$ ratios of 6, 10, and 20, respectively. The baseline results with lower and higher final mixing heights have predicted control requirements that are up to 4% lower and 2% higher than the ones with the median final mixing height. These results clearly indicate the importance of the initial $NMOC/NO_x$ ratio in EKMA analyses. For the baseline conditions, they indicate that the mixing height is moderately important.

The results for the runs with variations in the surface layer NMOC composition show large variations from the corresponding baseline results. For example, for the case with $NMOC/NO_x = 10$ and 1,000-meter final mixing height, the predicted control requirements were 45%, 66%, 50%, and 64% (versus 58% in the baseline run) for the low reactivity, high-reactivity, low-aldehyde, and high-aldehyde runs, respectively. The

TABLE 5-4

PREDICTED NMOC CONTROL REQUIREMENTS (%)

Case	NMOC/NO_x = 6			NMOC/NO_x = 10			NMOC/NO_x = 20		
	Mixing Height			Mixing Height			Mixing Height		
	500m	1000m	1500m	500m	1000m	1500m	500m	1000m	1500m
Baseline Case	26.8	29.1	30.1	53.7	57.7	59.2	77.4	80.1	81.0
Surface Layer NMOC:									
Low Reactivity	*	*	*	39.5	44.6	46.3	70.8	74.2	75.6
High Reactivity	37.3	41.6	43.2	62.0	65.8	67.0	81.3	83.5	84.3
Low Aldehydes	*	*	*	45.8	50.0	51.6	73.8	76.7	77.9
High Aldehydes	34.4	38.9	40.4	60.1	64.0	65.5	80.4	82.8	83.7
NMOC Aloft:									
10 ppbC	25.8	27.2	27.7	50.9	53.5	54.5	75.3	76.9	77.5
40 ppbC	26.6	28.6	29.4	53.0	56.6	58.0	76.9	79.3	80.2
150 ppbC	30.7	40.4	44.1	61.1	69.9	73.5	82.6	88.3	90.3
50 ppbC- High Aldehydes	27.5	30.6	31.9	55.0	60.1	61.7	78.3	81.4	82.5
50 ppbC- Low Reactivity	26.7	28.6	29.6	53.2	56.9	58.4	77.0	79.5	80.5
50 ppbC-High Reactivity	27.1	29.6	30.7	54.1	58.5	60.3	77.7	80.6	81.6
150 ppbC-High Aldehydes	35.4	49.6	54.9	65.6	77.2	81.26	85.4	92.5	94.9
Ozone Aloft = 0	23.5	23.2	23.3	45.3	44.7	44.5	71.5	70.8	70.7
30% Future NO_x Reduction	47.4	50.0	50.9	68.3	72.1	73.4	83.5	85.7	86.5
Without Emissions	41.1	45.8	47.4	64.5	68.2	69.6	82.5	84.7	85.5
Present Day Ozone:									
Ozone = .18 ppm	22.8	29.9	33.1	55.0	60.8	62.9	72.5	75.4	76.7
Ozone = .40 ppm	28.7	28.9	28.9	55.5	57.4	58.0	77.2	78.6	79.0
Initial Concentrations:									
HONO = 0		29.0			57.4			79.9	
HONO = 4 ppb		30.0			59.3			81.0	
PAN = 5 ppb		32.0			61.8			82.8	
Photolysis Rates:									
All Rates Decreased 20%		23.1			49.3			75.0	
NO2 Rate Decreased 20%		27.2			55.1			79.3	
HCHO Rate Decreased 20%		27.2			56.2			79.3	

---

*The solar radiation and NMOC were insufficient to generate the ozone design value

TABLE 5-5

RELATIVE CHANGE IN PREDICTED NMOC CONTROL REQUIREMENTS

Case	$NMOC/NO_x = 6$			$NMOC/NO_x = 10$			$NMOC/NO_x = 20$		
	Mixing Height			Mixing Height			Mixing Height		
	500m	1000m	1500m	500m	1000m	1500m	500m	1000m	1500m
Surface Layer NMOC:									
Low Reactivity	*	*	*	-.26	-.23	-.22	-.09	-.07	-.07
High Reactivity	.39	.43	.44	.15	.14	.13	.05	.04	.04
Low Aldehydes	*	*	*	-.15	-.13	-.13	-.05	-.04	-.04
High Aldehydes	.28	.34	.34	.12	.11	.11	.04	.03	.03
NMOC Aloft:									
10 ppbC	-.04	-.07	-.08	-.05	-.07	-.08	-.03	-.04	-.04
40 ppbC	-.01	-.02	-.02	-.01	-.02	-.02	-.01	-.01	-.01
150 ppbC	.15	.39	.47	.14	.21	.24	.07	.10	.11
50 ppbC- High Aldehydes	.03	.05	.06	.02	.04	.04	.01	.02	.02
50 ppbC- Low Reactivity	.00	-.02	-.02	-.01	-.01	-.01	-.01	-.01	-.01
50 ppbC-High Reactivity	.01	.02	.02	.01	.01	.02	.00	.01	.01
150 ppbC-High Aldehydes	.32	.70	.82	.22	.34	.37	.10	.15	.17
Ozone Aloft = 0	-.12	-.20	-.23	-.16	-.23	-.25	-.08	-.12	-.13
30% Future NO_x Reduction	.77	.72	.69	.27	.25	.24	.08	.07	.07
Without Emissions	.53	.57	.57	.20	.18	.18	.07	.06	.06
Present Day Ozone:									
Ozone = .18 ppm	-.15	.03	.10	.02	.05	.06	-.06	-.06	-.05
Ozone = .40 ppm	.07	-.01	-.04	.03	-.01	-.02	.00	-.02	-.02
Initial Concentrations:									
HONO = 0		.00			-.01			.00	
HONO = 4 ppb		.03			.03			.01	
PAN = 5 ppb		.10			.07			.03	
Photolysis Rates:									
All Rates Decreased 20%		-.21			-.15			-.06	
NO2 Rate Decreased 20%		-.07			-.05			-.01	
HCHO Rate Decreased 20%		-.07			-.03			-.01	

---

*The solar radiation and NMOC were insufficient to generate the ozone design value.

cases with lower and higher initial $NMOC/NO_x$ ratios showed more and less sensitivity to the reactivity of the surface layer NMOC, respectively. Solutions could not be obtained for the low-reactivity and low-aldehyde cases with an initial $NMOC/NO_x$ ratio of six because the lack of reactivity prevented reaching the present-day maximum ozone in the calculations. These results clearly indicate that NMOC reactivity of emissions and initial concentrations are very important inputs to the EKMA analysis. The results strongly support the recommendation made in Section 5 for using region-specific speciation data rather than default profiles whenever possible.

The results from the runs with variations in the NMOC aloft show several interesting features. First, as one would expect in any air quality model that incorporates entrainment of reactive pollutants, the importance of the concentrations of the entrained pollutants increases as the entrainment rate increases. This is shown by contrasting the relative changes in the control requirements for the runs with different final mixing heights (at any $NMOC/NO_x$ ratio). The higher the mixing height, the more important the NMOC aloft. Second, for these particular sets of runs, the magnitude of the NMOC concentration aloft is more important than variations in its composition. That is, the runs with alternate NMOC composition at 50 ppbC showed significantly smaller relative changes than the runs in which the NMOC concentration aloft ware varied. While not all of these variations may be equally probable, they still suggest that the concentration of NMOC aloft is probably more important than its composition. Its concentration aloft clearly is an important input to OZIPM and in the EKMA analysis.

The results from the runs with zero concentration for ozone aloft show the expected characteristics: 1) significantly lower control requirements since the ozone background is lower; 2) the importance of the ozone aloft value increases as the entrainment rate increases; and 3) with zero ozone aloft assumed, the NMOC control requirement is essentially independent of the mixing height.

The results for simulations with 30% reduction in future NO_x emissions show higher NMOC control requirements under all conditions. The increases in the control requirements under these conditions are generally greater than those for any other parameter variation investigated. The increase is especially large in the cases with the low initial NMOC/NO_x ratio. These results suggest significant attention should be given to the future NO_x emissions assumptions in EKMA analyses.

The predicted NMOC control requirements for the simulations without post-8 a.m. emissions (along the trajectory) are also higher than the corresponding baseline results. These results reflect the fact that control requirements generally increase as the NMOC/NO_x ratio increases. Without the emissions, which were assumed to have a lower NMOC/NO_x ratio than the initial concentrations, the effective NMOC/NO_x of the simulations is considerably higher. The influence of the emissions on the control requirement is especially large at the lower initial NMOC/NO_x ratio.

The control requirements predicted for the conditions with different present-day maximum ozone concentrations are somewhat counter-intuitive. The expected results for the cases with lower and higher present-day maximum ozone levels were lower and higher control requirements than those calculated for the baseline runs, respectively. However, the results show a mixture of moderately lower and higher control requirement predictions. Similar responses to this type of parameter variation have been reported in other modeling studies (e.g., see Carter 1981). One possible explanation of why higher present-day ozone maxima do not necessarily increase the control requirement is that ozone scavenging by NO_x becomes increasingly more important and effective as the absolute NO_x levels increase. However, this is quite speculative. For the purposes of this sensitivity analysis, these results indicate that the predicted control requirements are only moderately sensitivity to this input parameter.

The results of the simulations with 0 and 4 ppb of nitrous acid show this input has only minor effect on the predictions. Larger effects were expected since nitrous acid rapidly photolyzes to form the OH radical. However, even at 4 ppb, which is higher than is expected in all but the most polluted urban areas in the United States (Atkinson 1986), the initial nitrous acid had only a small effect on control requirements and, therefore, is not an important input to the model.

The results of the simulations with 5 ppb of initial PAN instead of zero in the baseline simulations show increased control requirements at all three NMOC/NO_x ratios. This occurs because PAN produces important radicals when it thermally decomposes, and the timing of its decomposition (under these conditions) effectively increases the reactivity of the mixture. PAN is considered a moderately important input to OZIPM; however, there is so little reliable ambient data that it is very difficult to objectively specify the initial concentration.

Lastly, the results with reduced photolysis indicate lower control requirements in all cases. Reductions in all of the photolytic rates have a much larger effect on the control requirements than comparable reductions in NO_2 or HCHO photolysis alone. Reduction in NO_2 photolysis rates alone was investigated because clouds are expected to attenuate the NO_2 photolysis rate more than the rate for other species. Overall, these results show the radiation inputs to OZIPM are moderately important for accurate estimates of the control requirements, particularly in cases with low initial NMOC/NO_x ratios.

In summary, this sensitivity analysis has identified the following parameters as most important in OZIPM applications with the updated mechanism:

- Initial NMOC/NO_x ratio
- NMOC reactivity
- Post-8 a.m. emissions along the trajectory
- Future NO_x emissions
- NMOC and ozone concentrations aloft

Meteorological information concerning the mixing heights and radiation levels are important inputs. Initial PAN concentrations are moderately important; however, initial nitrous acid concentration is unimportant. The composition of NMOC aloft also appears to be unimportant when the concentration is less than ~50 ppbC.

6. CONCLUSIONS

A surrogate species chemical mechanism for the photooxidation of NMOC and NO_x has been updated, thoroughly tested, and adapted for use in AQS models in this research program. The mechanism incorporates significant improvements in the understanding of photochemical smog formation in urban areas. Guidelines have been developed for using the mechanism in atmospheric modeling.

The mechanism evaluation is the most comprehensive study of its type on atmospheric chemical mechanisms. The evaluation is unique in that one mechanism was tested over a wide range of conditions using data from a large number of experiments. Consistent chamber characterization procedures were employed, and run-to-run adjustments of uncertain parameters were not permitted. Statistics on model performance were tabulated and displayed graphically. The performance data was examined closely for evidence of systematic biases.

The results of the mechanism evaluation indicate the mechanism is able to predict the rate of NO_x oxidation and maximum ozone concentrations with little bias and within ±30% error for a large number of single organic-NO_x experiments and organic mixture-NO_x experiments. The biases and average error in the maximum ozone predictions for the different types of experiments used in the testing program are summarized in Table 6-1. The results are statistically significant for propene, toluene, n-butane, and a large number of mixtures, including auto exhaust, for which there are many experiments. However, there is probably an insufficient number of experiments for the results for aldehydes, ketones, butenes, C5+ alkanes, and aromatics other than toluene to be statistically significant. The ozone predictions for single organic-NO_x irradiations with carbonyls, alkenes, and aromatics show good agreement with the data on the average. The results for alkanes are not satisfactory. They show a large amount of error. The uncertainty in chamber characterization procedures strongly affect the predictions for alkanes-NO_x mixtures. Because of these uncertainties, the alkane mechanism cannot be evaluated without ambiguity at this time. With the exception of the single alkane runs, the results show that the mechanism's bias is generally less than 10%. On the surrogate mixture

TABLE 6-1

AVERAGE MODEL PERFORMANCE FOR MAXIMUM OZONE

Run Type	Bias (%)	Error (%)
Formaldehyde	-1	19
Acetaldehyde	-26	26
Other Carbonyls	+4	44
All Carbonyls	-5	25
Ethene	+2	18
Propene	+3	18
Butenes	+4	34
All Alkenes	+3	21
Butane	+31	67
Branched Alkanes	+34	49
Long-chain Alkanes	+83	84
All Alkanes	+46	69
Benzene	+3	5
Toluene	+11	24
Xylenes	-9	16
Mesitylene	-11	21
All Aromatics	+1	19
All Single HC Runs	+12	33
Simple Mixtures	+10	35
Mini Surrogates	+10	22
Full Surrogates	+3	23
Auto Exhaust	-11	15
All HC Mixtures	+4	24
All Run Average	+7	28

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*Positive bias indicates model overprediction.

and auto exhaust runs, which are most representative of the types of mixtures for which the mechanism will be applied in atmospheric modeling, the average errors in the maximum ozone are ±23% and ±15%, respectively. This level of performance is good considering the uncertainties in both the chemistry and chamber characterization.

Model performance for other intermediate species, such as formaldehyde and peroxyacetylnitrate (PAN), is considerably worse than the performance for ozone; however, the data may not be reliable for these species.

In Phase II of the program, condensed versions of the mechanism employed in the testing program were developed for use in AQS models. Mechanisms were developed for use in single-cell models that can accommodate large chemical mechanisms and for use in multi-cell models that require fairly small chemical mechanisms. Very little mechanism condensation was required for the mechanism designed for use in single-cell models. Significant mechanism condensation assumptions were implemented in the mechanism designed for use in multi-cell models.

Predictions from the condensed versions of the mechanism were compared to predictions of the detailed mechanism for a range of mixtures and NMOC/NO_x ratios. The results showed that the single-cell model mechanism's predictions are almost identical (i.e., within ±2%) to the detailed mechanism's predictions for all of the key species. Predictions from the multi-cell model mechanism agree with those from the detailed mechanism within ±10% for all key species.

Information on speciation of organics for the classes in the mechanism was developed. First, a master list showing the assignment of individual organic compounds to organic classes in the mechanism was compiled. The uncertainty of each assignment was ranked, based on whether or not the surrogate species employed for the assigned class represents the reactivity of the individual species well. Second, ambient speciated NMOC data collected at the ground and above the mixed layer in the mornings in urban areas were analyzed. A default NMOC composition profile for emissions and ambient concentrations near the surface were developed from ambient data collected in 25 cities using a consistent measurement and speciation protocol. A default composition profile for NMOC aloft was compiled from aircraft data collected upwind of four cities. These default profiles can be used in atmospheric modeling applications where site-specific data are not available.

Sensitivity analysis was carried out using the updated chemical mechanism in the OZIPM AQS model. The sensitivity analysis was designed to identify the input parameter that most strongly influences the NMOC control requirements in EKMA analyses. Almost all of the sensitivity runs were performed at several NMOC/NO_x ratios and dilution rates since the sensitivity of model-to-parameter variations is known to depend on these parameters. The results of the analysis confirmed the importance of the following input parameters:

- NMOC/NO_x ratio
- NMOC composition
- Post-8 a.m. emissions rates along the trajectory
- Future changes in NO_x emission rates
- Ozone and NMOC concentrations aloft

Other relatively important parameters include the mixing height, radiation, and initial PAN concentrations. The results of the sensitivity analysis are intended to help air quality planners prioritize efforts for obtaining input data for the photochemical models used to develop control strategies.

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APPENDIX A

MECHANISM PERFORMANCE EVALUATION DATA

Table A-1

BACKGROUND AIR RUNS

Experiment	Maximum Concentration OZONE			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. UNC CHAMBER - PURE AIR				
JN0682R	0.203	0.218	0.016	0.08
OC0684R	0.097	0.101	0.004	0.04
OC0684B	0.119	0.113	-0.006	-0.05
Group Average	0.139	0.144	0.005	0.02
S. Dev.	0.056	0.065	0.011	0.07
Avg. Abs. Value			0.009	0.06
S. Dev.			0.006	0.02
2. SAPRC ITC - PURE AIR				
ITC940	0.072	0.077	0.005	0.07
ITC955	0.064	0.077	0.013	0.20
ITC1008	0.088	0.078	-0.009	-0.11
Group Average	0.075	0.077	0.003	0.05
S. Dev.	0.012	0.001	0.011	0.15
Avg. Abs. Value			0.009	0.12
S. Dev.			0.004	0.07

Table A-2

NOX-AIR and NOx-CO-AIR IRRADIATIONS

Experiment	Initial Concentrations			Final - Init NO			Final - Init NO2-UNC			Final - Init PROPENE		
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)
1. SAPRC EC - NOx-AIR												
EC436	1.79	0.0	0.0	-0.098	-0.049	0.049	-0.071	-0.060	0.011	-0.004	-0.005	-0.001
EC440	0.76	0.0	0.0	-0.063	-0.048	0.015	0.024	0.013	-0.011	-0.005	-0.005	0.000
EC442	0.58	0.0	0.1	0.069	0.092	0.023	-0.172	-0.160	0.012	-0.006	-0.005	0.001
EC457	0.50	0.0	0.1	-0.066	-0.043	0.023	0.008	-0.008	-0.016	-0.007	-0.008	-0.001
EC464	0.19	0.0	0.2	-0.019	-0.003	0.015	-0.002	-0.011	-0.009	-0.006	-0.007	-0.001
EC597	0.56	0.0	0.1	-0.061	-0.032	0.029	0.041	0.005	-0.036	-0.007	-0.006	0.000
EC599	3.40	0.0	0.0	2.276	1.890	-0.386	-2.685	-2.546	0.139	-0.007	-0.008	0.000
Group Average	1.11	0.0	0.1	0.291	0.258	-0.033	-0.408	-0.395	0.013	-0.006	-0.006	0.000
S. Dev.	1.13	0.0	0.1	0.877	0.721	0.156	1.007	0.950	0.058	0.001	0.001	0.001
Avg. Abs. Value				0.379	0.308	0.077	0.429	0.400	0.034	0.006	0.006	0.001
S. Dev.				0.837	0.698	0.137	0.996	0.948	0.047	0.001	0.001	0.000
2. SAPRC ITC - NOx-AIR												
ITC695	0.50	0.0	0.1	-0.021	-0.016	0.005	0.011	-0.002	-0.013	-0.003	-0.004	-0.001
ITC826	0.90	0.8	0.9	-0.349	-0.341	0.008	0.263	0.233	-0.030	-0.005	-0.005	0.000
ITC882	0.70	0.0	0.0	-0.001	-0.027	-0.026	-0.010	-0.014	-0.004	-0.001	-0.002	0.000
Group Average	0.70	0.3	0.3	-0.124	-0.128	-0.004	0.088	0.072	-0.016	-0.003	-0.003	0.000
S. Dev.	0.20	0.5	0.5	0.195	0.185	0.019	0.152	0.139	0.013	0.002	0.001	0.000
Avg. Abs. Value				0.124	0.128	0.013	0.095	0.083	0.016	0.003	0.003	0.000
S. Dev.				0.195	0.185	0.012	0.146	0.130	0.013	0.002	0.001	0.000
3. SAPRC OTC - NOx-AIR												
OTC185	0.28	0.0	0.1	-0.002	-0.004	-0.002	-0.003	0.000	0.002	-0.001	-0.002	-0.001
Group Average	0.28	0.0	0.1	-0.002	-0.004	-0.002	-0.003	0.000	0.002	-0.001	-0.002	-0.001
S. Dev.												
Avg. Abs. Value				0.002	0.004	0.002	0.003	0.000	0.002	0.001	0.002	0.001
S. Dev.												

TABLE A-2 (Continued)

Experiment	Initial Concentrations			Final - Init NO			Final - Init NO2-UNC			Final - Init PROPENE		
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)
4. UNC CHAMBER - NOx-AIR												
JN1782R	0.42	0.0	0.0	-0.061	-0.046	0.014	0.004	0.015	0.011			
JN1782B	0.42	0.0	0.0	-0.044	-0.042	0.002	0.003	0.011	0.008			
JN2782B	0.44	0.0	0.0	-0.113	-0.085	0.028	0.050	0.046	-0.004			
AU0282R	0.39	0.0	0.0	0.035	0.044	0.009	-0.129	-0.090	0.039			
AU2082R	0.41	0.0	0.0	-0.011	-0.001	0.010	-0.049	-0.035	0.014			
AU2282R	0.46	0.0	0.0	0.000	0.028	0.028	-0.147	-0.089	0.058			
AU2382R	0.43	0.0	0.0	0.056	0.059	0.003	-0.144	-0.098	0.046			
OC0882R	0.30	0.0	0.0	-0.024	-0.035	-0.011	0.005	0.029	0.024			
OC0882B	0.30	0.0	0.0	-0.017	-0.035	-0.017	0.009	0.030	0.021			
ST0582R	0.50	0.0	0.0	0.070	0.073	0.003	-0.171	-0.127	0.044			
JL2483R	0.31	0.0	0.0	-0.047	-0.032	0.015	0.011	0.006	-0.005			
JL2483B	0.48	0.0	0.0	-0.071	-0.047	0.024	0.014	0.007	-0.007			
JL2783B	0.43	0.0	0.0	-0.090	-0.056	0.034	0.036	0.021	-0.015			
AU0683B	0.37	0.0	0.0	0.001	0.013	0.012	-0.090	-0.047	0.043			
Group Average	0.40	0.0	0.0	-0.023	-0.012	0.011	-0.043	-0.023	0.020			
S. Dev.	0.06	0.0	0.0	0.053	0.048	0.015	0.077	0.057	0.023			
Avg. Abs. Value				0.046	0.043	0.015	0.062	0.047	0.024			
S. Dev.				0.034	0.022	0.010	0.062	0.039	0.018			
5. SAPRC ITC - NOx-CO-AIR												
ITC625	0.28	0.0	0.1	-0.069	-0.084	-0.015	0.068	0.077	0.009	-0.004	-0.004	0.000
ITC634	0.60	0.0	0.1	-0.040	-0.059	-0.019	0.034	0.050	0.015	-0.004	-0.002	0.001
Group Average	0.44	0.0	0.1	-0.055	-0.071	-0.017	0.051	0.063	0.012	-0.004	-0.003	0.001
S. Dev.	0.22	0.0	0.0	0.021	0.018	0.003	0.024	0.019	0.005	0.000	0.001	0.001
Avg. Abs. Value				0.055	0.071	0.017	0.051	0.063	0.012	0.004	0.003	0.001
S. Dev.				0.021	0.018	0.003	0.024	0.019	0.005	0.000	0.001	0.001
6. SAPRC OTC - NOx-CO-AIR												
OTC188	0.34	0.0	0.1	-0.090	-0.126	-0.036	0.072	0.115	0.043	-0.003	-0.002	0.001
OTC201A	0.37	0.0	0.1	-0.160	-0.146	0.014	0.162	0.133	-0.029	-0.004	-0.003	0.001
OTC201B	0.76	0.0	0.1	-0.123	-0.104	0.019	0.096	0.090	-0.006	-0.004	-0.002	0.002
Group Average	0.49	0.0	0.1	-0.124	-0.125	-0.001	0.110	0.113	0.003	-0.004	-0.003	0.001
S. Dev.	0.23	0.0	0.0	0.035	0.021	0.030	0.046	0.021	0.037	0.001	0.001	0.001
Avg. Abs. Value				0.124	0.125	0.023	0.110	0.113	0.026	0.004	0.003	0.001
S. Dev.				0.035	0.021	0.011	0.046	0.021	0.019	0.001	0.001	0.001

TABLE A-2 (Continued)

Experiment	Initial Concentrations			Final - Init NO			Final - Init NO2-UNC			Final - Init PROPENE		
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)
7. UNC CHAMBER - NOx-CO-AIR												
JN2782R	0.45	0.0	0.0	-0.320	-0.272	0.047	0.202	0.229	0.027			
AU0282B	0.40	0.0	0.0	-0.054	-0.040	0.015	-0.002	-0.012	-0.010			
AU2082B	0.41	0.0	0.0	-0.111	-0.097	0.013	0.072	0.059	-0.013			
AU2282B	0.46	0.0	0.0	-0.086	-0.076	0.010	0.003	0.011	0.008			
AU2382B	0.43	0.0	0.0	-0.004	-0.024	-0.020	-0.042	-0.018	0.023			
ST0582B	0.50	0.0	0.0	0.019	-0.010	-0.030	-0.086	-0.046	0.040			
JL2783R	0.47	0.0	0.0	-0.289			0.214					
AU0683R	0.39	0.0	0.0	-0.133			0.032					
Group Average	0.44	0.0	0.0	-0.122	-0.087	0.006	0.049	0.037	0.013			
S. Dev.	0.04	0.0	0.0	0.124	0.097	0.028	0.109	0.100	0.021			
Avg. Abs. Value				0.127	0.087	0.023	0.082	0.063	0.020			
S. Dev.				0.118	0.097	0.014	0.083	0.084	0.012			

Table A-3

FORMALDEHYDE - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Half-Life HCHO			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
1. SAPRC EC - FORMALDEHYDE-AIR											
EC250	0.02	0.3	14.5	0.215	0.258	0.043	0.20	130	119	-11	-0.08
EC255	0.02	0.3	20.4	0.203	0.253	0.051	0.25	126	117	-9	-0.07
Group Average	0.02	0.3	17.4	0.209	0.256	0.047	0.23	128	118	-10	-0.08
S. Dev.	0.00	0.0	4.2	0.009	0.003	0.005	0.03	2	1	1	0.01
Avg. Abs. Value						0.047	0.23			10	0.08
S. Dev.						0.005	0.03			1	0.01
2. UNC CHAMBER - FORMALDEHYDE-AIR											
JL1782R	0.01	0.5	71.2	0.239	0.349	0.110	0.46	255	161	-94	-0.37
JL1782B	0.01	0.6	86.0	0.264	0.332	0.067	0.26	246	194	-52	-0.21
OC0784R	0.00	0.4	96.1	0.087	0.255	0.168	1.94	415	170	-245	-0.59
OC0784B	0.01	1.0	125.7	0.138	0.348	0.210	1.52	445	220	-225	-0.51
OC1684R	0.00	0.4		0.153	0.277	0.124	0.81	263	182	-81	-0.31
OC1684B	0.00	0.3		0.133	0.227	0.094	0.70	268	168	-100	-0.37
Group Average	0.00	0.5	94.8	0.169	0.298	0.129	0.95	315	182	-132	-0.39
S. Dev.	0.00	0.3	23.0	0.068	0.052	0.052	0.65	89	21	81	0.14
Avg. Abs. Value						0.129	0.95			132	0.39
S. Dev.						0.052	0.65			81	0.14

TABLE A-4

ACETALDEHYDE - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Maximum Concentration PAN			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - ACETALDEHYDE-AIR											
EC253	0.02	1.1	53.8	0.137	0.130	-0.007	-0.05	0.040	0.044	0.004	0.10
Group Average	0.02	1.1	53.8	0.137	0.130	-0.007	-0.05	0.040	0.044	0.004	0.10
S. Dev.											
Avg. Abs. Value						0.007	0.05			0.004	0.10
S. Dev.											
2. SAPRC ITC - ACETALDEHYDE-AIR											
ITC627	0.03	0.8	26.1	0.060	0.066	0.006	0.10	0.013	0.014	0.001	0.05
ITC636	0.03	0.7	26.6	0.047	0.067	0.020		0.011	0.014	0.003	0.24
ITC825	0.00	0.0			0.021				0.008		
ITC957	0.04	1.1	27.6	0.076	0.069	-0.007	-0.10	0.013	0.015	0.003	0.23
ITC974	0.03	0.9	29.8	0.085	0.064	-0.021	-0.24	6.300	0.015	-6.285	-1.00
ITC1009	0.04	0.9	27.0	0.078	0.069	-0.009	-0.12	0.008	0.014	0.006	0.74
Group Average	0.03	0.7	27.4	0.069	0.059	-0.002	-0.09	1.269	0.013	-1.255	0.05
S. Dev.	0.01	0.4	1.4	0.015	0.019	0.016	0.14	2.812	0.003	2.812	0.64
Avg. Abs. Value						0.013	0.14			1.260	0.45
S. Dev.						0.007	0.07			2.810	0.40

TABLE A-4 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Maximum Concentration PAN			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
3. SAPRC OTC - ACETALDEHYDE-AIR											
OTC200A	0.01	1.1	96.9	0.088	0.071	-0.017	-0.19	0.008	0.007	-0.001	-0.12
OTC200B	0.01	0.8	68.8	0.076	0.070	-0.006	-0.08	0.006	0.007	0.001	0.21
OTC206A	0.01	1.3	136.8	0.030	0.053	0.024		0.020	0.010	-0.010	-0.48
OTC206B	0.01	1.0	94.0	0.023	0.076	0.053		0.013	0.009	-0.004	-0.30
OTC234A	0.04	1.0	26.2	0.083	0.122	0.039	0.47	0.004	0.011	0.007	1.75
OTC234B	0.04	1.5	39.3	0.084	0.123	0.039	0.47	0.007	0.011	0.004	0.63
Group Average	0.02	1.1	77.0	0.064	0.086	0.022	0.17	0.010	0.009	0.000	0.28
S. Dev.	0.01	0.2	40.8	0.029	0.029	0.028	0.35	0.006	0.002	0.006	0.82
Avg. Abs. Value						0.030	0.30			0.005	0.58
S. Dev.						0.017	0.20			0.003	0.60
4. UNC CHAMBER - ACETALDEHYDE-AIR											
JL2683R	0.02	1.1	48.3	0.422	0.413	-0.008	-0.02	0.026	0.054	0.028	1.09
JL2683B	0.01	1.1	87.6	0.331	0.290	-0.041	-0.12	0.027	0.061	0.034	1.23
AU0483R	0.03	1.0	34.3	0.548	0.459	-0.089	-0.16	0.040	0.054	0.014	0.34
AU0483B	0.02	1.1	47.1	0.431	0.382	-0.049	-0.11	0.040	0.066	0.026	0.66
OC1584R	0.02	0.0	1.1	0.140	0.222	0.082	0.58	0.023	0.066	0.043	1.83
OC1584B	0.02	0.0	1.1	0.193	0.266	0.073	0.38	0.035	0.065	0.030	0.85
Group Average	0.02	0.7	36.6	0.344	0.339	-0.005	0.09	0.032	0.061	0.029	1.00
S. Dev.	0.01	0.5	32.8	0.155	0.093	0.069	0.31	0.007	0.006	0.010	0.52
Avg. Abs. Value						0.057	0.23			0.029	1.00
S. Dev.						0.030	0.21			0.010	0.52

Table A-5

FORMALDEHYDE - NOx RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt				Half-Life FORMALDEHYDE			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
1. SAPRC EC - FORMALDEHYDE															
EC251	0.11	0.2	1.7	0.271	0.302	0.031	0.11	3.25	4.16	0.91	0.28	112	76	-36	-0.32
EC252	0.49	0.4	0.7	0.032	0.023	-0.009		1.94	2.23	0.30	0.15	99	141	42	0.42
EC389	4.75	9.1	1.9	0.002	0.030	0.027		50.01	52.98	2.97	0.06	190	104	-86	-0.45
EC391	4.43	17.7	4.0	2.371	2.592	0.221	0.09	102.89	104.14	1.25	0.01	75	89	14	0.19
EC392	8.05	9.5	1.2	0.000	0.008	0.007		13.52	31.53	18.02	1.33	129	124	-5	-0.04
Group Average	3.57	7.4	1.9	0.535	0.591	0.056	0.10	34.32	39.01	4.69	0.37	121	106	-14	-0.04
S. Dev.	3.30	7.3	1.3	1.032	1.125	0.094	0.01	42.99	42.01	7.52	0.55	43	26	49	0.36
Avg. Abs. Value						0.059	0.10			4.69	0.37			36	0.28
S. Dev.						0.091	0.01			7.52	0.55			31	0.17
2. SAPRC ITC - FORMALDEHYDE															
ITC864	0.54	0.1	0.1	0.001	0.018	0.017		0.60	0.73	0.13	0.21				
Group Average	0.54	0.1	0.1					0.60	0.73	0.13	0.21				
S. Dev.															
Avg. Abs. Value										0.13	0.21				
S. Dev.															
3. SAPRC OTC - FORMALDEHYDE															
OTC235A	0.56	0.1	0.1	0.273	0.171	-0.102	-0.37	2.00	1.80	-0.20	-0.10				
OTC235B	0.58	0.1	0.1	0.308	0.249	-0.059	-0.19	2.16	2.06	-0.09	-0.04				
Group Average	0.57	0.1	0.1	0.291	0.210	-0.081	-0.28	2.08	1.93	-0.15	-0.07				
S. Dev.	0.02	0.0	0.0	0.025	0.055	0.030	0.13	0.11	0.19	0.08	0.04				
Avg. Abs. Value						0.081	0.28			0.15	0.07				
S. Dev.						0.030	0.13			0.08	0.04				

TABLE A-5 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt				Half-Life FORMALDEHYDE			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
4. UNC CHAMBER - FORMALDEHYDE															
AU0179B	0.35	1.0	2.8	0.618	0.492	-0.126	-0.20	2.06	2.40	0.34	0.17	245	181	-64	-0.26
AU0279B	0.21	1.0	4.7	0.606	0.562	-0.044	-0.07	2.12	2.91	0.79	0.37	233	150	-83	-0.36
AU0479B	0.23	0.5	2.1	0.378	0.281	-0.097	-0.26	1.17	1.23	0.06	0.05	280	189	-91	-0.32
AU0579B	0.54	1.2	2.2	0.508	0.490	-0.018	-0.04	1.95	2.56	0.61	0.31	283	198	-85	-0.30
JL2381B	0.43	1.5	3.5	0.637	0.709	0.072	0.11	2.70	3.43	0.73	0.27	205	182	-23	-0.11
OC0984R	0.56	1.0	1.7	0.666	1.038	0.372	0.56	2.11	2.82	0.71	0.34	328	226	-102	-0.31
OC0984B	0.50	1.0	1.9	0.301	0.334	0.033	0.11	1.51	1.83	0.32	0.21	330	213	-117	-0.35
Group Average	0.40	1.0	2.7	0.531	0.558	0.027	0.03	1.94	2.45	0.51	0.25	272	191	-80	-0.29
S. Dev.	0.14	0.3	1.1	0.141	0.255	0.167	0.27	0.49	0.73	0.27	0.11	47	24	30	0.08
Avg. Abs. Value						0.109	0.19			0.51	0.25			80	0.29
S. Dev.						0.122	0.18			0.27	0.11			30	0.08

Table A-6

ALDEHYDE OR KETONE - NOx - Air RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - ACETALDEHYDE											
EC164	0.51	0.7	1.4	0.086	0.063	-0.023	-0.27	2.03	1.71	-0.32	-0.16
EC254	0.11	1.0	8.5	0.264	0.243	-0.020	-0.08	1.33	1.28	-0.05	-0.04
Group Average	0.31	0.8	5.0	0.175	0.153	-0.022	-0.17	1.68	1.49	-0.19	-0.10
S. Dev.	0.28	0.2	5.0	0.126	0.128	0.002	0.13	0.49	0.31	0.19	0.08
Avg. Abs. Value						0.022	0.17			0.19	0.10
S. Dev.						0.002	0.13			0.19	0.08
2. UNC CHAMBER - ACETALDEHYDE											
AU0179R	0.36	2.0	5.7	0.930	0.729	-0.201	-0.22	1.98	1.67	-0.30	-0.15
JN1482R	0.31	3.1	9.9	0.731	0.461	-0.270	-0.37	1.62	1.40	-0.22	-0.14
AU2482B	0.32	1.9	6.0	0.972	0.634	-0.338	-0.35	1.68	1.39	-0.29	-0.17
Group Average	0.33	2.3	7.2	0.878	0.608	-0.270	-0.31	1.76	1.49	-0.27	-0.15
S. Dev.	0.02	0.7	2.3	0.129	0.136	0.069	0.08	0.19	0.16	0.04	0.02
Avg. Abs. Value						0.270	0.31			0.27	0.15
S. Dev.						0.069	0.08			0.04	0.02
3. UNC CHAMBER - PROPANALDEHYDE											
JN1482B	0.30	3.1	10.5	0.733	0.459	-0.274	-0.37	1.75	1.49	-0.26	-0.15
AU2482R	0.33	1.9	5.6	0.941	0.609	-0.331	-0.35	1.82	1.41	-0.41	-0.22
Group Average	0.32	2.5	8.0	0.837	0.534	-0.303	-0.36	1.79	1.45	-0.33	-0.19
S. Dev.	0.02	0.9	3.4	0.147	0.106	0.040	0.02	0.05	0.05	0.11	0.05
Avg. Abs. Value						0.303	0.36			0.33	0.19
S. Dev.						0.040	0.02			0.11	0.05

TABLE A-6 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
4. UNC CHAMBER - ACETONE											
JN0480R	0.17	4.8	27.5	0.233	0.516	0.283	1.21	0.48	0.72	0.24	0.50
Group Average	0.17	4.8	27.5	0.233	0.516	0.283	1.21	0.48	0.72	0.24	0.50
S. Dev.											
Avg. Abs. Value						0.283	1.21			0.24	0.50
S. Dev.											
5. UNC CHAMBER - METHYL ETHYL KETONE											
OC2079R	0.22	13.6	60.5	0.563	0.457	-0.106	-0.19	1.25	1.16	-0.09	-0.07
JN0480B	0.18	3.8	21.6	0.652	0.602	-0.050	-0.08	1.13	1.08	-0.05	-0.04
Group Average	0.20	8.7	41.0	0.607	0.530	-0.078	-0.13	1.19	1.12	-0.07	-0.06
S. Dev.	0.03	6.9	27.5	0.063	0.103	0.040	0.08	0.09	0.06	0.03	0.02
Avg. Abs. Value						0.078	0.13			0.07	0.06
S. Dev.						0.040	0.08			0.03	0.02

Table A-7

N-BUTANE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - BUTANE											
EC130	0.10	17.6	179.3	0.459	0.498	0.039	0.08	4.41	2.86	-1.56	-0.35
EC133	0.50	8.6	17.1	0.249	0.075	-0.174	-0.70	2.42	1.30	-1.12	-0.46
EC134	0.51	8.3	16.3	0.034	0.058	0.024		0.94	1.52	0.58	0.62
EC137	0.50	8.7	17.3	0.042	0.070	0.028		1.02	1.54	0.52	0.51
EC162	0.51	8.2	16.3	0.112	0.082	-0.031	-0.27	1.73	1.50	-0.23	-0.13
EC163	0.49	9.0	18.3	0.454	0.227	-0.227	-0.50	3.31	2.17	-1.14	-0.34
EC168	0.49	8.0	16.2	0.655	0.446	-0.209	-0.32	2.03	1.54	-0.49	-0.24
EC178	0.10	7.8	79.6	0.384	0.443	0.059	0.15	1.61	1.77	0.16	0.10
EC304	0.47	17.1	36.7	0.362	0.617	0.255	0.71	2.09	2.78	0.70	0.33
EC305	0.10	15.7	159.7	0.398	0.597	0.199	0.50	2.39	3.66	1.27	0.53
EC306	0.19	25.8	138.2	0.535	0.746	0.211	0.39	2.38	4.16	1.78	0.75
EC307	0.10	25.8	252.9	0.420	0.651	0.231	0.55	2.61	6.10	3.49	1.34
EC308	0.48	16.2	33.6	0.047	0.210	0.164		1.04	2.58	1.54	1.49
EC309	0.47	17.2	36.3	0.545	0.751	0.206	0.38	2.00	3.16	1.16	0.58
Group Average	0.36	13.9	72.7	0.335	0.391	0.055	0.09	2.14	2.62	0.48	0.34
S. Dev.	0.19	6.4	77.7	0.205	0.263	0.167	0.47	0.94	1.34	1.36	0.61
Avg. Abs. Value						0.147	0.41			1.12	0.56
S. Dev.						0.089	0.20			0.85	0.41
2. SAPRC ITC - BUTANE											
ITC507	0.09	15.2	165.0	0.149	0.399	0.251	1.68	0.69	1.42	0.74	1.07
ITC533	0.12	11.9	99.8	0.165	0.466	0.301	1.83	0.61	1.82	1.21	1.99
ITC770	0.52	37.9	72.8	0.042	0.149	0.107		1.56	3.83	2.27	1.45
ITC939	0.51	14.8	28.9	0.017	0.039	0.022		0.36	0.86	0.49	1.37
ITC948	0.26	10.0	38.2	0.054	0.142	0.088	1.64	0.53	1.05	0.52	0.97
Group Average	0.30	18.0	81.0	0.085	0.239	0.154	1.72	0.75	1.80	1.05	1.37
S. Dev.	0.21	11.4	54.8	0.067	0.183	0.117	0.10	0.47	1.20	0.74	0.40
Avg. Abs. Value						0.154	1.72			1.05	1.37
S. Dev.						0.117	0.10			0.74	0.40

TABLE A-7 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
3. SAPRC OTC - BUTANE											
OTC211	0.55	42.8	77.5	0.008	0.098	0.090		0.56	1.11	0.55	0.97
Group Average	0.55	42.8	77.5					0.56	1.11	0.55	0.97
S. Dev.											
Avg. Abs. Value										0.55	0.97
S. Dev.											
4. UNC CHAMBER - BUTANE											
JL2178R	0.24	7.2	29.9	0.763	0.447	-0.316	-0.41	1.17	0.96	-0.21	-0.18
JL2178B	0.24	15.4	63.9	0.986	0.812	-0.175	-0.18	1.64	1.41	-0.23	-0.14
JL2278R	0.55	7.9	14.4	0.166	0.051	-0.115	-0.69	0.90	0.69	-0.21	-0.24
JL2278B	0.55	17.5	31.5	0.788	0.218	-0.570	-0.72	1.55	1.05	-0.50	-0.32
ST1879B	0.21	21.2	103.1	0.185	0.267	0.081	0.44	0.51	0.64	0.13	0.26
OC0979R	0.21	14.6	71.0	0.191	0.359	0.168	0.88	0.60	0.81	0.21	0.36
OC1879B	0.20	14.3	71.8	0.208	0.419	0.211	1.01	0.60	0.82	0.22	0.37
Group Average	0.31	14.0	55.1	0.470	0.367	-0.102	0.05	1.00	0.91	-0.08	0.01
S. Dev.	0.16	5.0	31.0	0.359	0.238	0.281	0.73	0.47	0.26	0.27	0.30
Avg. Abs. Value						0.234	0.62			0.25	0.27
S. Dev.						0.166	0.29			0.12	0.09

TABLE A-7 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration ACETALD				Maximum Concentration MEK			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - BUTANE												
EC130	0.044	0.053	0.009	0.21	0.130	0.190	0.060	0.46	0.165	0.199	0.034	0.21
EC133	0.031	0.006	-0.025	-0.80	0.096	0.085	-0.011	-0.11	0.122	0.078	-0.044	-0.36
EC134	0.004	0.005	0.001	0.17	0.049	0.080	0.031	0.64	0.064	0.073	0.009	0.14
EC137	0.005	0.005	0.000	0.08	0.062	0.083	0.021	0.33	0.072	0.075	0.003	0.04
EC162	0.015	0.006	-0.009	-0.58	0.098	0.085	-0.013	-0.13	0.067	0.078	0.011	0.16
EC163	0.106	0.050	-0.055	-0.52	0.526	0.410	-0.116	-0.22	0.077	0.065	-0.013	-0.16
EC168	0.092	0.055	-0.037	-0.41	0.114	0.115	0.001	0.01	0.193	0.142	-0.051	-0.27
EC178	0.045	0.056	0.011	0.24	0.092	0.114	0.023	0.25	0.091	0.136	0.045	0.50
EC304	0.027	0.064	0.037	1.34	0.149	0.203	0.054	0.37	0.092	0.210	0.118	1.28
EC305	0.031	0.056	0.025	0.80	0.131	0.189	0.058	0.44	0.085	0.191	0.107	1.26
EC306	0.035	0.072	0.037	1.03	0.166	0.248	0.082	0.49	0.098	0.254	0.156	1.59
EC307	0.026	0.055	0.029	1.09	0.161	0.242	0.081	0.51	0.139	0.235	0.096	0.69
EC308	0.005	0.018	0.013	2.79	0.037	0.082	0.045	1.23	0.076	0.159	0.083	1.08
EC309	0.034	0.065	0.031	0.91	0.226	0.263	0.037	0.16	0.115	0.167	0.052	0.45
Group Average	0.036	0.041	0.005	0.45	0.145	0.171	0.025	0.32	0.104	0.147	0.043	0.47
S. Dev.	0.030	0.026	0.028	0.96	0.121	0.097	0.051	0.38	0.039	0.065	0.062	0.62
Avg. Abs. Value			0.023	0.78			0.045	0.38			0.059	0.58
S. Dev.			0.016	0.69			0.032	0.30			0.047	0.51
2. SAPRC ITC - BUTANE												
ITC507	0.004	0.012	0.008	2.06	0.029	0.108	0.078	2.69	0.075	0.092	0.017	0.23
ITC533	0.004	0.024	0.020	4.62	0.033	0.118	0.085	2.57	0.036	0.110	0.073	2.01
ITC770	0.000	0.005	0.005		0.056	0.137	0.081	1.45	0.047	0.106	0.059	1.27
ITC939		0.001			0.014	0.076	0.062	4.41	0.019	0.061	0.042	2.25
ITC948		0.005			0.015	0.072	0.058	3.89	0.021	0.061	0.040	1.94
Group Average	0.003	0.009	0.011	3.34	0.029	0.102	0.073	3.00	0.040	0.086	0.047	1.54
S. Dev.	0.002	0.009	0.008	1.81	0.017	0.028	0.012	1.17	0.023	0.024	0.021	0.82
Avg. Abs. Value			0.011	3.34			0.073	3.00			0.047	1.54
S. Dev.			0.008	1.81			0.012	1.17			0.021	0.82

TABLE A-7 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration ACETALD				Maximum Concentration MEK			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
3. SAPRC OTC - BUTANE												
OTC211	0.013	0.003	-0.010	-0.80	0.100	0.117	0.017	0.17		0.107		
Group Average	0.013	0.003	-0.010	-0.80	0.100	0.117	0.017	0.17				
S. Dev.												
Avg. Abs. Value			0.010	0.80			0.017	0.17				
S. Dev.												
4. UNC CHAMBER - BUTANE												
JL2178R						0.001				0.001		
JL2178B						0.001				0.002		
JL2278R						0.000				0.001		
JL2278B						0.001				0.001		
ST1879B	0.010	0.013	0.004	0.40								
OC0979R	1.100	0.015	-1.085	-0.99					0.000	0.106	0.106	
OC1879B	4.590	0.021	-4.569	-1.00					0.052	0.117	0.064	1.22
Group Average	1.900	0.016	-1.884	-0.53					0.026	0.038	0.085	1.22
S. Dev.	2.393	0.004	2.389	0.80								
Avg. Abs. Value			1.886	0.79							0.085	1.22
S. Dev.			2.386	0.34								

TABLE A-8

BRANCHED ALKANE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - 2,3 DIMETHYL BUTANE											
EC165	0.10	11.3	114.3	0.488	0.671	0.182	0.37	1.77	999.00		
EC169	0.19	4.5	23.5	0.493	0.528	0.035	0.07	1.00	1.21	0.22	0.22
EC171	0.10	3.5	35.7	0.403	0.472	0.069	0.17	1.30	1.33	0.03	0.02
Group Average	0.13	6.4	57.8	0.462	0.557	0.095	0.20	1.36	333.85	0.12	0.12
S. Dev.	0.05	4.2	49.3	0.051	0.102	0.077	0.15	0.39	576.04	0.13	0.14
Avg. Abs. Value						0.095	0.20			0.12	0.12
S. Dev.						0.077	0.15			0.13	0.14
2. UNC CHAMBER - 2,3 DIMETHYL BUTANE											
OC1879R	0.20	16.4	81.9	0.236	0.556	0.320	1.36	0.64	0.93	0.30	0.47
OC2079B	0.22	12.6	56.5	0.217	0.416	0.199	0.92	0.66	0.90	0.25	0.37
Group Average	0.21	14.5	69.2	0.226	0.486	0.259	1.14	0.65	0.92	0.27	0.42
S. Dev.	0.02	2.7	18.0	0.014	0.099	0.086	0.31	0.02	0.02	0.04	0.07
Avg. Abs. Value						0.259	1.14			0.27	0.42
S. Dev.						0.086	0.31			0.04	0.07
3. UNC CHAMBER - ISO PENTANE											
AU1983R	0.38	4.7	12.6	0.088	0.074	-0.014	-0.16	0.61	0.63	0.02	0.03
Group Average	0.38	4.7	12.6	0.088	0.074	-0.014	-0.16	0.61	0.63	0.02	0.03
S. Dev.											
Avg. Abs. Value						0.014	0.16			0.02	0.03
S. Dev.											
4. UNC CHAMBER - ISO OCTANE											
AU1983B	0.37	4.1	10.9	0.057	0.035	-0.022	-0.38	0.53	0.51	-0.02	-0.04
Group Average	0.37	4.1	10.9	0.057	0.035	-0.022	-0.38	0.53	0.51	-0.02	-0.04
S. Dev.											
Avg. Abs. Value						0.022	0.38			0.02	0.04
S. Dev.											

Table A-9

PENTANE AND HIGHER N-ALKANES - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - PENTANE											
EC135	0.10	20.4	212.7	0.435	0.576	0.141	0.32	2.92	2.96	0.05	0.02
Group Average	0.10	20.4	212.7	0.435	0.576	0.141	0.32	2.92	2.96	0.05	0.02
S. Dev.											
Avg. Abs. Value						0.141	0.32			0.05	0.02
S. Dev.											
2. UNC CHAMBER - PENTANE											
OC0979B	0.21	15.1	73.3	0.184	0.309	0.126	0.68	0.59	0.75	0.16	0.27
Group Average	0.21	15.1	73.3	0.184	0.309	0.126	0.68	0.59	0.75	0.16	0.27
S. Dev.											
Avg. Abs. Value						0.126	0.68			0.16	0.27
S. Dev.											
3. SAPRC EC - HEXANE											
EC131	0.10	24.6	251.1	0.393	0.561	0.168	0.43	1.92	2.17	0.25	0.13
Group Average	0.10	24.6	251.1	0.393	0.561	0.168	0.43	1.92	2.17	0.25	0.13
S. Dev.											
Avg. Abs. Value						0.168	0.43			0.25	0.13
S. Dev.											
4. SAPRC ITC - HEXANE											
ITC559	0.19	279.4	1441.1	0.377	0.571	0.194	0.51	1.79	1.77	-0.02	-0.01
Group Average	0.19	279.4	1441.1	0.377	0.571	0.194	0.51	1.79	1.77	-0.02	-0.01
S. Dev.											
Avg. Abs. Value						0.194	0.51			0.02	0.01
S. Dev.											

TABLE A-9 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
5. SAPRC ITC - HEPTANE											
ITC538	0.11	60.3	529.0	0.150	0.364	0.213	1.42	0.74	1.21	0.47	0.64
ITC540	0.11	274.8	2421.3	0.360	0.436	0.076	0.21	1.85	1.28	-0.57	-0.31
Group Average	0.11	167.6	1475.2	0.255	0.400	0.145	0.82	1.30	1.25	-0.05	0.17
S. Dev.	0.00	151.7	1338.1	0.148	0.051	0.097	0.85	0.79	0.05	0.74	0.67
Avg. Abs. Value						0.145	0.82			0.52	0.48
S. Dev.						0.097	0.85			0.07	0.24
6. SAPRC ITC - OCTANE											
ITC552	0.13	428.8	3278.4	0.315	0.314	-0.002	-0.01	1.19	1.02	-0.17	-0.14
ITC761	0.52	75.2	145.9	0.030	0.049	0.020		1.08	1.63	0.55	0.51
ITC762	0.27	74.7	280.4	0.105	0.240	0.134	1.27	0.83	2.06	1.23	1.48
ITC763	0.28	7.7	27.7	0.041	0.118	0.077		0.68	2.39	1.71	2.51
ITC797	0.52	7.3	14.0	0.004	0.009	0.005		0.64	0.92	0.28	0.44
Group Average	0.34	118.7	749.3	0.099	0.146	0.047	0.63	0.88	1.60	0.72	0.96
S. Dev.	0.17	176.6	1417.9	0.126	0.128	0.058	0.90	0.24	0.64	0.75	1.04
Avg. Abs. Value						0.047	0.64			0.79	1.02
S. Dev.						0.057	0.90			0.66	0.97
7. UNC CHAMBER - OCTANE											
ST1879R	0.21	6.3	30.4	0.122	0.467	0.346	2.83	0.40	0.63	0.23	0.58
Group Average	0.21	6.3	30.4	0.122	0.467	0.346	2.83	0.40	0.63	0.23	0.58
S. Dev.											
Avg. Abs. Value						0.346	2.83			0.23	0.58
S. Dev.											
8. SAPRC EC - NONANE											
EC155	0.10	37.3	385.1	0.264	0.438	0.174	0.66	1.33	1.07	-0.26	-0.20
Group Average	0.10	37.3	385.1	0.264	0.438	0.174	0.66	1.33	1.07	-0.26	-0.20
S. Dev.											
Avg. Abs. Value						0.174	0.66			0.26	0.20
S. Dev.											

Table A-10

ETHENE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt				Half-Life ETHENE			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
1. SAPRC EC - ETHENE															
EC142	0.48	1.9	4.1	0.782	0.563	-0.218	-0.28	3.20	2.50	-0.70	-0.22	222	290	68	0.31
EC143	0.50	4.1	8.1	1.087	0.850	-0.237	-0.22	8.50	5.48	-3.02	-0.36	155	228	73	0.47
EC156	0.50	4.0	8.0	1.105	0.808	-0.297	-0.27	8.89	5.46	-3.43	-0.39	153	228	75	0.49
EC285	1.01	3.9	3.9	0.840	1.063	0.223	0.27	5.05	6.07	1.03	0.20	265	248	-17	-0.06
EC286	0.94	7.5	8.0	1.081	1.271	0.190	0.18	11.76	14.13	2.37	0.20	174	162	-12	-0.07
EC287	0.53	8.0	15.1	0.965	1.098	0.133	0.14	13.89	17.07	3.19	0.23	171	155	-16	-0.09
Group Average	0.66	4.9	7.9	0.977	0.942	-0.034	-0.03	8.55	8.45	-0.09	-0.05	190	218	28	0.17
S. Dev.	0.25	2.4	4.1	0.139	0.252	0.240	0.25	3.99	5.75	2.76	0.30	44	51	47	0.28
Avg. Abs. Value						0.216	0.22			2.29	0.27			43	0.25
S. Dev.						0.054	0.06			1.16	0.08			31	0.20
2. SAPRC ITC - ETHENE															
ITC926	0.51	7.9	15.6	0.982	0.993	0.011	0.01	6.96	8.50	1.54	0.22	227	225	-2	-0.01
ITC936	0.50	3.9	7.8	0.940	0.950	0.010	0.01	2.72	3.39	0.67	0.25	337	310	-27	-0.08
Group Average	0.50	5.9	11.7	0.961	0.971	0.010	0.01	4.84	5.95	1.11	0.23	282	267	-14	-0.04
S. Dev.	0.01	2.8	5.5	0.030	0.031	0.001	0.00	3.00	3.62	0.61	0.02	77	60	17	0.05
Avg. Abs. Value						0.010	0.01			1.11	0.23			14	0.04
S. Dev.						0.001	0.00			0.61	0.02			17	0.05
3. UNC CHAMBER - ETHENE															
AU0479R	0.23	0.9	3.9	0.729	0.555	-0.174	-0.24	1.60	1.15	-0.45	-0.28	307	389	82	0.27
AU0579R	0.64	4.1	6.4	1.294	1.108	-0.186	-0.14	3.17	3.08	-0.09	-0.03	333	367	34	0.10
OC0584R	0.36	3.2	8.8	0.856	1.007	0.151	0.18	2.16	2.44	0.28	0.13	394	321	-73	-0.19
OC1184R	0.35	2.9	8.2	0.858	1.102	0.244	0.28	2.22	2.48	0.26	0.12	366	305	-61	-0.17
OC1284R	0.72	2.7	3.7	0.495	0.576	0.082	0.16	1.58	1.65	0.07	0.04		485		
OC0584B	0.37	1.8	5.0	0.675	0.778	0.103	0.15	1.48	1.61	0.13	0.09	465	387	-78	-0.17
Group Average	0.45	2.6	6.0	0.818	0.854	0.037	0.07	2.04	2.07	0.03	0.01	373	375	-19	-0.03
S. Dev.	0.19	1.1	2.2	0.269	0.254	0.177	0.21	0.64	0.72	0.27	0.15	61	63	72	0.20
Avg. Abs. Value						0.157	0.19			0.21	0.11			65	0.18
S. Dev.						0.059	0.06			0.14	0.09			19	0.06

Table A-10 (Continued)

Experiment	Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - ETHENE				
EC142	0.207	0.385	0.177	0.85
EC143	0.967	0.758	-0.209	-0.22
EC156	0.735	0.753	0.018	0.02
EC285	0.709	0.740	0.031	0.04
EC286	1.425	1.342	-0.083	-0.06
EC287	1.426	1.275	-0.151	-0.11
Group Average	0.912	0.876	-0.036	0.09
S. Dev.	0.469	0.365	0.140	0.39
Avg. Abs. Value			0.111	0.22
S. Dev.			0.079	0.32
2. SAPRC ITC - ETHENE				
ITC926	1.308	1.223	-0.085	-0.06
ITC936	0.697	0.682	-0.015	-0.02
Group Average	1.002	0.953	-0.050	-0.04
S. Dev.	0.432	0.383	0.049	0.03
Avg. Abs. Value			0.050	0.04
S. Dev.			0.049	0.03
3. UNC CHAMBER - ETHENE				
AU0479R	0.306	0.152	-0.153	-0.50
AU0579R	1.488	0.663	-0.825	-0.55
OC0584R	0.869	0.525	-0.344	-0.40
OC1184R	0.707	0.484	-0.223	-0.32
OC1284R	0.655	0.447	-0.207	-0.32
OC0584B	0.558	0.308	-0.249	-0.45
Group Average	0.764	0.430	-0.334	-0.42
S. Dev.	0.401	0.178	0.249	0.10
Avg. Abs. Value			0.334	0.42
S. Dev.			0.249	0.10

Table A-11

PROPENE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt				Half-Life PROPENE			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
1. SAPRC EC - PROPENE															
EC121	0.51	1.5	2.9	0.506	0.491	-0.014	-0.03	7.46	4.11	-3.36	-0.45	56	114	58	1.04
EC177	0.46	1.5	3.2	0.540	0.498	-0.042	-0.08	3.89	3.91	0.02	0.01	95	119	24	0.25
EC216	0.52	1.5	3.0	0.564	0.595	0.031	0.05	4.18	5.63	1.45	0.35	105	91	-14	-0.13
EC217	0.48	0.6	1.2	0.149	0.273	0.124	0.83	0.80	1.47	0.68	0.85	116	124	8	0.07
EC230	0.52	1.9	3.7	0.344	0.310	-0.035	-0.10	3.06	4.76	1.70	0.56	123	125	2	0.02
EC256	0.56	0.4	0.7	0.002	0.010	0.007		0.98	1.01	0.03	0.03	181	175	-6	-0.03
EC257	0.56	0.7	1.3	0.068	0.104	0.035	0.52	3.35	4.16	0.81	0.24	80	77	-3	-0.04
EC276	0.52	1.6	3.2	0.388	0.459	0.071	0.18	3.24	4.39	1.15	0.35	128	123	-5	-0.04
EC277	0.11	1.7	15.7	0.313	0.397	0.085	0.27	8.27	7.48	-0.80	-0.10	74	67	-7	-0.09
EC278	0.49	3.1	6.2	0.625	0.683	0.057	0.09	7.72	9.42	1.69	0.22	87	82	-5	-0.06
EC279	0.97	3.5	3.5	0.679	0.703	0.024	0.04	6.64	8.69	2.04	0.31	123	114	-9	-0.07
EC314	0.93	3.2	3.5	0.728	0.813	0.085	0.12	7.21	10.98	3.77	0.52	98	85	-13	-0.13
EC315	0.94	2.9	3.1	0.344	0.567	0.223	0.65	4.33	6.68	2.35	0.54	159	126	-33	-0.21
EC316	0.98	3.2	3.3	0.955	1.000	0.045	0.05	10.64	12.08	1.44	0.14	70	75	5	0.07
EC317	0.54	1.5	2.8	0.615	0.615	-0.001	0.00	4.06	4.48	0.42	0.10	85	78	-7	-0.08
Group Average	0.61	1.9	3.8	0.455	0.501	0.046	0.18	5.06	5.95	0.89	0.24	105	105	0	0.04
S. Dev.	0.24	1.0	3.5	0.260	0.260	0.067	0.28	2.81	3.24	1.61	0.31	33	28	20	0.30
Avg. Abs. Value						0.059	0.21			1.45	0.32			13	0.16
S. Dev.						0.056	0.26			1.10	0.23			14	0.25
2. SAPRC ITC - PROPENE															
ITC693	0.49	3.5	7.2	0.779	0.713	-0.066	-0.09	5.07	6.82	1.76	0.35	126	110	-16	-0.13
ITC810	0.52	2.8	5.4	0.782	0.703	-0.080	-0.10	4.25	4.75	0.50	0.12	135	141	6	0.04
ITC860	0.52	3.0	5.8	0.585	0.662	0.078	0.13	3.57	5.08	1.51	0.42	142	131	-11	-0.08
ITC925	0.54	2.8	5.2	0.779	0.715	-0.064	-0.08	3.72	4.13	0.41	0.11	150	147	-3	-0.02
ITC938	0.52	2.1	4.0	0.729	0.517	-0.212	-0.29	3.61	2.70	-0.91	-0.25	137	185	48	0.35
ITC947	0.53	1.9	3.6	0.710	0.533	-0.177	-0.25	3.34	2.67	-0.67	-0.20	157	188	31	0.20
ITC960	0.50	2.6	5.2	0.721	0.641	-0.080	-0.11	4.23	3.91	-0.32	-0.07	133	148	15	0.11
Group Average	0.52	2.7	5.2	0.726	0.641	-0.086	-0.11	3.97	4.29	0.33	0.07	140	150	10	0.07
S. Dev.	0.02	0.5	1.2	0.070	0.084	0.093	0.14	0.59	1.45	1.03	0.26	10	28	23	0.17
Avg. Abs. Value						0.108	0.15			0.87	0.22			18	0.13
S. Dev.						0.060	0.08			0.56	0.13			15	0.11

Table A-11 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt				Half-Life PROPENE			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
3. SAPRC OTC - PROPENE															
OTC186	0.55	3.6	6.6	0.822	0.845	0.023	0.03	5.16	6.47	1.30	0.25	104	108	4	0.04
OTC191	0.54	3.7	6.9	0.903	1.057	0.154	0.17	12.18	11.19	-0.99	-0.08	56	70	14	0.25
OTC210	0.57	2.7	4.8	0.972	0.969	-0.003	0.00	6.70	5.57	-1.13	-0.17	121	127	6	0.05
OTC233	0.46	0.1	0.2	0.633	0.913	0.280	0.44	3.69	4.80	1.11	0.30	132	129	-3	-0.02
OTC236	0.53	3.3	6.3	0.848	0.968	0.120	0.14	6.91	7.43	0.52	0.08	109	102	-7	-0.06
Group Average	0.53	2.7	5.0	0.836	0.950	0.115	0.16	6.93	7.09	0.16	0.08	104	107	2	0.05
S. Dev.	0.04	1.5	2.8	0.127	0.078	0.113	0.18	3.21	2.49	1.15	0.20	29	23	8	0.12
Avg. Abs. Value						0.116	0.16			1.01	0.18			6	0.08
S. Dev.						0.111	0.17			0.29	0.10			4	0.09
4. UNC CHAMBER - PROPENE															
JA1078R	0.46	3.1	6.9	0.363	0.445	0.082	0.22	0.46	0.50	0.03	0.07	867			
OC1278B	0.48	1.4	2.9	0.461	0.390	-0.072	-0.16	1.40	1.74	0.34	0.25	303	241	-62	-0.20
OC2078R	0.46	1.3	2.9	0.340	0.307	-0.033	-0.10	1.23	1.48	0.25	0.21	341	263	-78	-0.23
OC2078B	0.46	3.5	7.7	0.727	0.852	0.124	0.17	2.83	3.59	0.76	0.27	233	180	-53	-0.23
OC2178R	0.50	3.9	7.9	0.670	0.801	0.131	0.20	2.53	3.55	1.02	0.40	251	187	-64	-0.25
OC2578B	0.44	1.3	2.9	0.230	0.251	0.021	0.09	1.03	1.40	0.37	0.36	347	265	-82	-0.24
JN1279R	0.50	1.0	2.1	0.382	0.245	-0.137	-0.36	0.85	0.79	-0.06	-0.07	327	316	-11	-0.03
JN1279B	0.49	1.5	3.0	0.673	0.413	-0.260	-0.39	1.24	1.03	-0.20	-0.17	320	331	11	0.03
JN1379R	0.45	2.9	6.5	0.974	0.776	-0.197	-0.20	2.69	2.91	0.22	0.08	254	226	-28	-0.11
AU0279R	0.22	1.5	7.0	0.788	0.548	-0.240	-0.30	2.41	2.07	-0.34	-0.14	166	188	22	0.13
AU2780B	0.48	1.9	4.0	1.044	0.996	-0.048	-0.05	3.26	3.22	-0.04	-0.01	212	219	7	0.03
ST0482B	0.23	1.1	4.9	0.658	0.587	-0.071	-0.11	1.46	1.63	0.17	0.12	266	216	-50	-0.19
ST1382B	0.33	1.1	3.3	0.731	0.598	-0.133	-0.18	1.69	1.55	-0.14	-0.08	236	237	1	0.00
JL1783R	0.27	1.1	3.9	0.848	0.620	-0.228	-0.27	2.10	1.63	-0.47	-0.22	194	234	40	0.21
JL2183R	0.22	1.1	5.0	0.804	0.676	-0.128	-0.16	1.76	1.70	-0.06	-0.04	225	212	-13	-0.06
JL2983B	0.21	1.1	5.3	0.697	0.651	-0.045	-0.06	1.66	1.77	0.11	0.07	235	209	-26	-0.11
JL3183R	0.21	1.1	5.1	0.719	0.617	-0.102	-0.14	1.81	1.44	-0.37	-0.20	150	169	19	0.13
ST2383B	0.38	1.6	4.3	0.405	0.616	0.211	0.52	1.23	2.03	0.81	0.66	347	221	-126	-0.36
OC0484R	0.36	2.1	5.9	0.645	0.732	0.087	0.14	2.07	2.33	0.26	0.13	293	208	-85	-0.29
OC0484B	0.36	1.0	2.9	0.446	0.446	0.000	0.00	1.25	1.34	0.09	0.07	319	250	-69	-0.22
OC1184B	0.36	2.2	6.3	0.674	0.735	0.061	0.09	2.38	2.66	0.28	0.12	235	187	-48	-0.20
OC1284B	0.68	2.0	2.9	0.432	0.402	-0.030	-0.07	1.67	1.86	0.19	0.12	352	285	-67	-0.19
Group Average	0.39	1.8	4.7	0.623	0.577	-0.046	-0.05	1.77	1.92	0.15	0.09	294	230	-36	-0.11
S. Dev.	0.12	0.9	1.8	0.214	0.199	0.128	0.22	0.70	0.83	0.37	0.21	141	42	43	0.16
Avg. Abs. Value						0.111	0.18			0.30	0.17			45	0.16
S. Dev.						0.076	0.12			0.26	0.15			32	0.10

Table A-11 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration ACETALD				Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - PROPENE												
EC121	0.167	0.155	-0.011	-0.07	0.162	0.210	0.048	0.29	0.278	0.228	-0.050	-0.18
EC177	0.165	0.180	0.015	0.09	0.186	0.216	0.030	0.16	0.091	0.232	0.142	1.56
EC216	0.154	0.197	0.043	0.28	0.202	0.222	0.021	0.10	0.181	0.264	0.082	0.45
EC217	0.019	0.037	0.018	0.99	0.151	0.150	-0.001	-0.01	0.040	0.077	0.037	0.91
EC230	0.110	0.041	-0.069	-0.63	0.260	0.242	-0.017	-0.07	0.282	0.316	0.034	0.12
EC256	0.001	0.001	0.000	-0.24	0.040	0.044	0.004	0.11	0.042	0.057	0.014	0.34
EC257	0.007	0.010	0.003	0.40	0.037	0.049	0.012	0.32		0.547		
EC276	0.100	0.141	0.042	0.42	0.192	0.237	0.045	0.24	0.192	0.256	0.064	0.33
EC277	0.077	0.109	0.031	0.40	0.192	0.260	0.068	0.35	0.213	0.244	0.032	0.15
EC278	0.260	0.261	0.001	0.01	0.378	0.464	0.087	0.23	0.438	0.481	0.043	0.10
EC279	0.340	0.326	-0.014	-0.04	0.470	0.510	0.040	0.08	0.522	0.539	0.017	0.03
EC314	0.226	0.373	0.147	0.65	0.441	0.475	0.034	0.08	0.523	0.511	-0.012	-0.02
EC315	0.116	0.280	0.164	1.42	0.382	0.420	0.038	0.10	0.383	0.405	0.022	0.06
EC316	0.270	0.319	0.049	0.18	0.489	0.481	-0.008	-0.02	0.586	0.542	-0.044	-0.08
EC317	0.130	0.194	0.064	0.49	0.205	0.217	0.013	0.06	0.268	0.229	-0.039	-0.15
Group Average	0.143	0.175	0.032	0.29	0.252	0.280	0.027	0.14	0.288	0.328	0.024	0.26
S. Dev.	0.100	0.120	0.060	0.50	0.146	0.154	0.028	0.13	0.179	0.165	0.052	0.47
Avg. Abs. Value			0.045	0.42			0.031	0.15			0.045	0.32
S. Dev.			0.050	0.39			0.024	0.11			0.034	0.43
2. SAPRC ITC - PROPENE												
ITC693	0.311	0.256	-0.055	-0.18	0.320	0.536	0.215	0.67	0.416	0.505	0.089	0.21
ITC810	0.140	0.238	0.098	0.70	0.174	0.448	0.274	1.57	0.447	0.416	-0.032	-0.07
ITC860		0.216			0.189	0.439	0.250	1.33	0.617	0.411	-0.206	-0.33
ITC925	0.205	0.233	0.028	0.13	0.141	0.441	0.300	2.13	0.467	0.408	-0.059	-0.13
ITC938	0.296	0.143	-0.153	-0.52	0.134	0.334	0.200	1.49	0.416	0.298	-0.117	-0.28
ITC947	0.270	0.138	-0.132	-0.49	0.121	0.333	0.213	1.76	0.004	0.296	0.292	73.04
ITC960	0.056	0.201	0.146	2.62	0.203	0.414	0.211	1.04	0.255	0.383	0.127	0.50
Group Average	0.213	0.204	-0.011	0.38	0.183	0.421	0.238	1.43	0.375	0.388	0.014	10.42
S. Dev.	0.100	0.046	0.122	1.19	0.068	0.071	0.038	0.48	0.195	0.073	0.168	27.62
Avg. Abs. Value			0.102	0.77			0.238	1.43			0.132	10.65
S. Dev.			0.051	0.93			0.038	0.48			0.090	27.51

Table A-11 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration ACETALD				Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
3. SAPRC OTC - PROPENE												
OTC186	0.260	0.293	0.033	0.13	0.508	0.597	0.089	0.18	0.462	0.573	0.112	0.24
OTC191	0.190	0.261	0.071	0.37	0.433	0.571	0.138	0.32	0.811	0.549	-0.262	-0.32
OTC210	0.126	0.185	0.059	0.47	0.481	0.481	0.000	0.00		0.473		
OTC233	0.037	0.127	0.090	2.42	0.380	0.472	0.092	0.24		0.456		
OTC236	0.095	0.258	0.163	1.72	0.599	0.569	-0.030	-0.05	0.459	0.544	0.085	0.19
Group Average	0.142	0.225	0.083	1.02	0.480	0.538	0.058	0.14	0.577	0.519	-0.022	0.03
S. Dev.	0.086	0.068	0.049	1.00	0.082	0.057	0.070	0.16	0.202	0.051	0.208	0.31
Avg. Abs. Value			0.083	1.02			0.070	0.16			0.153	0.25
S. Dev.			0.049	1.00			0.055	0.13			0.095	0.07
4. UNC CHAMBER - PROPENE												
JA1078R						0.003				0.001		
OC1278B	0.069	0.094	0.025	0.37	0.214	0.185	-0.029	-0.14				
OC2078R	0.082	0.078	-0.003	-0.04	0.190	0.188	-0.002	-0.01	0.440	0.162	-0.278	-0.63
OC2078B	0.241	0.286	0.045	0.19	0.460	0.526	0.066	0.14	0.800	0.495	-0.305	-0.38
OC2178R	0.162	0.273	0.111	0.69	0.455	0.510	0.055	0.12	0.840	0.476	-0.364	-0.43
OC2578B	0.050	0.063	0.013	0.27	0.166	0.170	0.005	0.03		0.144		
JN1279R	0.032	0.037	0.005	0.16	0.122	0.107	-0.015	-0.13	0.142	0.088	-0.054	-0.38
JN1279B	0.134	0.133	-0.001	-0.01	0.385	0.389	0.004	0.01	0.208	0.098	-0.110	-0.53
JN1379R	0.223	0.270	0.047	0.21	0.419	0.396	-0.023	-0.05	0.410	0.379	-0.031	-0.07
AU0279R		0.103			0.201	0.209	0.007	0.04	0.440	0.215	-0.225	-0.51
AU2780B	0.130	0.151	0.022	0.17		0.279			0.030	0.258	0.228	7.61
ST0482B	0.122	0.129	0.007	0.06		0.162				0.158		
ST1382B	0.117	0.106	-0.011	-0.10		0.153				0.152		
JL1783R	0.086	0.099	0.013	0.15	0.134	0.154	0.020	0.15	0.174	0.163	-0.012	-0.07
JL2183R	0.093	0.092	-0.001	-0.01	0.124	0.156	0.032	0.26	0.214	0.166	-0.048	-0.22
JL2983B	0.092	0.119	0.027	0.30	0.129	0.156	0.026	0.20	0.185	0.157	-0.028	-0.15
JL3183R	0.088	0.109	0.021	0.24	0.134	0.149	0.014	0.11	0.211	0.154	-0.058	-0.27
ST2383B	0.100	0.202	0.102	1.03	0.215	0.232	0.017	0.08		0.212		
OC0484R	0.167	0.208	0.041	0.25	0.293	0.300	0.007	0.02	0.424	0.290	-0.135	-0.32
OC0484B	0.086	0.087	0.001	0.01	0.145	0.143	-0.002	-0.02	0.223	0.134	-0.089	-0.40
OC1184B	0.180	0.224	0.045	0.25	0.287	0.326	0.039	0.14	0.484	0.312	-0.171	-0.35
OC1284B	0.144	0.119	-0.025	-0.17	0.236	0.272	0.037	0.16	0.427	0.246	-0.181	-0.42
Group Average	0.120	0.142	0.024	0.20	0.239	0.235	0.014	0.06	0.353	0.212	-0.116	0.15
S. Dev.	0.054	0.073	0.034	0.27	0.117	0.130	0.025	0.11	0.226	0.123	0.141	1.99
Avg. Abs. Value			0.028	0.23			0.022	0.10			0.145	0.80
S. Dev.			0.031	0.24			0.018	0.07			0.110	1.82

Table A-12

BUTENE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - 1-BUTENE											
EC122	0.50	0.9	1.7	0.227	0.115	-0.112	-0.49	2.29	1.64	-0.65	-0.28
EC123	0.51	1.6	3.2	0.506	0.315	-0.190	-0.38	4.16	2.61	-1.55	-0.37
EC124	0.99	1.7	1.7	0.247	0.189	-0.058	-0.23	1.99	2.09	0.10	0.05
Group Average	0.67	1.4	2.2	0.326	0.206	-0.120	-0.37	2.81	2.11	-0.70	-0.20
S. Dev.	0.28	0.5	0.9	0.155	0.101	0.067	0.13	1.18	0.48	0.83	0.22
Avg. Abs. Value						0.120	0.37			0.77	0.24
S. Dev.						0.067	0.13			0.73	0.17
2. SAPRC ITC - 1-BUTENE											
ITC927	0.31	3.8	12.3	0.646	0.713	0.067	0.10	3.24	4.66	1.42	0.44
ITC928	0.67	3.9	5.8	0.022	0.088	0.066		1.36	2.05	0.70	0.51
ITC930	0.32	7.3	22.6	0.717	0.795	0.078	0.11	7.91	12.21	4.30	0.54
ITC935	0.66	7.5	11.4	0.872	0.918	0.046	0.05	5.39	8.17	2.78	0.52
Group Average	0.49	5.6	13.0	0.564	0.629	0.064	0.09	4.47	6.77	2.30	0.50
S. Dev.	0.20	2.0	7.0	0.374	0.370	0.013	0.03	2.82	4.41	1.59	0.04
Avg. Abs. Value						0.064	0.09			2.30	0.50
S. Dev.						0.013	0.03			1.59	0.04
3. SAPRC EC - TRANS-2-BUTENE											
EC146	0.51	0.9	1.8	0.247	0.149	-0.098	-0.40	5.87	3.85	-2.02	-0.34
EC147	0.98	1.7	1.7	0.154	0.117	-0.037	-0.24	9.83	7.43	-2.40	-0.24
EC157	0.53	0.9	1.7	0.205	0.127	-0.078	-0.38	5.96	3.60	-2.36	-0.40
Group Average	0.67	1.2	1.7	0.202	0.131	-0.071	-0.34	7.22	4.96	-2.26	-0.33
S. Dev.	0.27	0.5	0.1	0.046	0.016	0.031	0.09	2.26	2.14	0.21	0.08
Avg. Abs. Value						0.071	0.34			2.26	0.33
S. Dev.						0.031	0.09			0.21	0.08

Table A-12 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
4. UNC CHAMBER - TRANS-2-BUTENE											
ST2783B	0.43	2.0	4.7	0.523	0.457	-0.067	-0.13	3.00	3.03	0.02	0.01
Group Average	0.43	2.0	4.7	0.523	0.457	-0.067	-0.13	3.00	3.03	0.02	0.01
S. Dev.											
Avg. Abs. Value						0.067	0.13			0.02	0.01
S. Dev.											
5. SAPRC ITC - ISO BUTENE											
ITC694	0.51	4.6	9.1	0.900	0.984	0.085	0.09	8.84	15.06	6.22	0.70
Group Average	0.51	4.6	9.1	0.900	0.984	0.085	0.09	8.84	15.06	6.22	0.70
S. Dev.											
Avg. Abs. Value						0.085	0.09			6.22	0.70
S. Dev.											

Table A-13

BENZENE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC ITC - BENZENE											
ITC560	0.12	332.3	2874.4	0.323	0.349	0.026	0.08	7.01	9.61	2.60	0.37
ITC561	0.11	79.1	694.2	0.273	0.292	0.020	0.07	4.75	4.40	-0.36	-0.07
ITC562	0.56	83.8	149.7	0.412	0.391	-0.020	-0.05	2.85	3.04	0.19	0.07
ITC698	0.50	83.5	167.4	0.374	0.379	0.005	0.01	2.87	3.68	0.81	0.28
ITC710	0.55	83.6	151.0	0.367	0.387	0.020	0.05	2.70	3.49	0.79	0.29
ITC831	1.01	12.2	12.1	0.021	0.005	-0.016		0.17	0.29	0.12	0.71
Group Average	0.47	112.4	674.8	0.295	0.300	0.006	0.03	3.39	4.08	0.69	0.27
S. Dev.	0.33	111.3	1103.2	0.142	0.150	0.020	0.05	2.30	3.06	1.03	0.27
Avg. Abs. Value						0.018	0.05			0.81	0.30
S. Dev.						0.007	0.03			0.92	0.24

Table A-14

TOLUENE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - TOLUENE											
EC264	0.48	8.1	17.0	0.419	0.425	0.006	0.01	4.46	5.05	0.59	0.13
EC265	0.48	7.5	15.6	0.393	0.419	0.026	0.07	3.56	4.83	1.28	0.36
EC266	0.49	8.4	17.0	0.405	0.429	0.024	0.06	4.62	5.21	0.58	0.13
EC269	0.47	4.0	8.4	0.318	0.267	-0.051	-0.16	2.55	2.43	-0.12	-0.05
EC270	0.46	4.2	9.0	0.369	0.392	0.023	0.06	3.72	3.93	0.20	0.05
EC271	0.21	8.0	37.4	0.296	0.339	0.043	0.15	6.56	5.80	-0.77	-0.12
EC272	0.48	4.1	8.5	0.410	0.264	-0.147	-0.36	3.69	2.44	-1.25	-0.34
EC273	0.11	4.1	37.2	0.215	0.259	0.044	0.21	5.90	3.69	-2.21	-0.37
EC327	0.45	4.0	8.9	0.376	0.355	-0.021	-0.06	2.49	2.58	0.09	0.04
EC336	0.44	7.2	16.3	0.396	0.478	0.082	0.21	6.06	6.98	0.92	0.15
EC337	0.45	7.9	17.7	0.325	0.350	0.025	0.08	2.55	2.66	0.11	0.04
EC339	0.44	5.0	11.3	0.225	0.145	-0.080	-0.35	1.53	1.50	-0.04	-0.02
EC340	0.43	4.1	9.5	0.344	0.326	-0.018	-0.05	2.50	2.43	-0.07	-0.03
Group Average	0.42	5.9	16.5	0.345	0.342	-0.003	-0.01	3.86	3.81	-0.05	0.00
S. Dev.	0.12	1.9	9.9	0.068	0.091	0.061	0.18	1.58	1.64	0.92	0.20
Avg. Abs. Value						0.045	0.14			0.63	0.14
S. Dev.						0.038	0.11			0.65	0.13
2. SAPRC ITC - TOLUENE											
ITC699	0.51	10.5	20.8	0.485	0.506	0.022	0.05	4.72	5.42	0.70	0.15
ITC828	1.02	3.0	3.0	0.021	0.006	-0.015		0.49	1.18	0.69	1.39
Group Average	0.76	6.8	11.9	0.253	0.256	0.004	0.05	2.61	3.30	0.69	0.77
S. Dev.	0.36	5.3	12.6					2.99	3.00	0.01	0.88
Avg. Abs. Value						0.018	0.05			0.69	0.77
S. Dev.										0.01	0.88
3. UNC CHAMBER - TOLUENE											
JL3080R	0.18	3.9	21.3	0.273	0.374	0.100	0.37	1.20	1.22	0.03	0.02
AU2780R	0.48	2.3	4.8	0.736	0.548	-0.187	-0.25	1.76	1.40	-0.36	-0.21
AU2782B	0.43	3.0	7.0	0.116	0.134	0.018	0.15	0.63	0.71	0.08	0.12
OC2782R	0.39	4.5	11.7	0.123	0.341	0.218	1.78	0.66	0.93	0.27	0.41
AU0183R	0.39	4.6	11.8	0.458	0.492	0.034	0.07	1.75	1.65	-0.10	-0.06
Group Average	0.37	3.7	11.3	0.341	0.378	0.037	0.42	1.20	1.18	-0.02	0.06
S. Dev.	0.11	1.0	6.4	0.261	0.161	0.148	0.79	0.55	0.37	0.23	0.23
Avg. Abs. Value						0.111	0.53			0.17	0.16
S. Dev.						0.090	0.71			0.14	0.15

Table A-14 (Continued)

Experiment	Maximum Concentration PAN			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - TOLUENE				
EC264	0.071	0.087	0.017	0.23
EC265	0.072	0.084	0.012	0.17
EC266	0.075	0.090	0.015	0.20
EC269	0.050	0.037	-0.013	-0.25
EC270	0.057	0.059	0.002	0.03
EC271	0.053	0.062	0.009	0.18
EC272	0.132	0.037	-0.095	-0.72
EC273	0.032	0.042	0.010	0.31
EC327	0.041	0.048	0.007	0.18
EC336	0.059	0.081	0.022	0.37
EC337	0.047	0.059	0.012	0.26
EC339	0.024	0.016	-0.008	-0.32
EC340	0.042	0.040	-0.002	-0.04
Group Average	0.058	0.057	-0.001	0.05
S. Dev.	0.027	0.023	0.030	0.31
Avg. Abs. Value			0.017	0.25
S. Dev.			0.024	0.17
2. SAPRC ITC - TOLUENE				
ITC699	0.145	0.107	-0.038	-0.26
ITC828	0.000	0.001	0.001	
Group Average	0.072	0.054	-0.018	-0.26
S. Dev.				
Avg. Abs. Value			0.019	0.26
S. Dev.				
3. UNC CHAMBER - TOLUENE				
JL3080R	0.037	0.038	0.002	0.05
AU2780R	0.020	0.012	-0.008	-0.41
AU2782B	0.012	0.009	-0.002	-0.21
OC2782R	0.013	0.062	0.049	3.65
AU0183R	0.043	0.049	0.005	0.12
Group Average	0.025	0.034	0.009	0.64
S. Dev.	0.014	0.023	0.023	1.70
Avg. Abs. Value			0.013	0.89
S. Dev.			0.020	1.55

Table A-15

XYLENE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - XYLENE											
EC343	0.28	4.2	14.9	0.283	0.374	0.090	0.32	8.18	10.44	2.26	0.28
EC344	0.67	4.0	5.9	0.589	0.524	-0.064	-0.11	10.72	9.63	-1.10	-0.10
EC345	0.28	3.7	13.3	0.396	0.383	-0.013	-0.03	11.35	10.64	-0.71	-0.06
EC346	0.26	3.9	14.8	0.384	0.369	-0.015	-0.04	7.65	10.57	2.92	0.38
Group Average	0.37	3.9	12.2	0.413	0.412	0.000	0.03	9.48	10.32	0.84	0.12
S. Dev.	0.20	0.2	4.3	0.128	0.075	0.065	0.19	1.83	0.47	2.04	0.24
Avg. Abs. Value						0.046	0.12			1.75	0.21
S. Dev.						0.038	0.13			1.02	0.15
2. SAPRC ITC - XYLENE											
ITC702	0.52	4.0	7.8	0.627	0.478	-0.149	-0.24	7.79	8.99	1.20	0.15
ITC827	1.07	1.2	1.1	0.021	0.010	-0.010		1.12	1.96	0.84	0.74
Group Average	0.79	2.6	4.4	0.324	0.244	-0.080	-0.24	4.45	5.47	1.02	0.45
S. Dev.	0.39	2.0	4.7					4.71	4.97	0.26	0.42
Avg. Abs. Value						0.080	0.24			1.02	0.45
S. Dev.										0.26	0.42
3. UNC CHAMBER - XYLENE											
JL3080B	0.18	2.2	12.4	0.555	0.397	-0.158	-0.28	1.97	1.88	-0.09	-0.05
AU2782R	0.43	2.0	4.6	0.491	0.451	-0.039	-0.08	1.31	1.32	0.02	0.01
OC2782B	0.39	2.8	7.0	0.396	0.387	-0.009	-0.02	1.43	1.61	0.18	0.12
AU0183B	0.37	2.7	7.2	0.688	0.460	-0.228	-0.33	2.39	1.48	-0.91	-0.38
Group Average	0.34	2.4	7.8	0.532	0.424	-0.108	-0.18	1.77	1.57	-0.20	-0.07
S. Dev.	0.11	0.4	3.3	0.123	0.037	0.102	0.15	0.50	0.23	0.48	0.22
Avg. Abs. Value						0.108	0.18			0.30	0.14
S. Dev.						0.102	0.15			0.41	0.17

Table A-15 (Continued)

Experiment	Maximum Concentration PAN			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - XYLENE				
EC343	0.081	0.107	0.027	0.33
EC344	0.175	0.171	-0.004	-0.02
EC345	0.107	0.106	-0.001	-0.01
EC346	0.102	0.101	-0.001	-0.01
Group Average	0.116	0.121	0.005	0.07
S. Dev.	0.041	0.033	0.014	0.17
Avg. Abs. Value			0.008	0.09
S. Dev.			0.012	0.16
2. SAPRC ITC - XYLENE				
ITC702	0.390	0.155	-0.235	-0.60
ITC827	0.002	0.003	0.001	0.26
Group Average	0.196	0.079	-0.117	-0.17
S. Dev.	0.274	0.108	0.166	0.61
Avg. Abs. Value			0.118	0.43
S. Dev.			0.166	0.24
3. UNC CHAMBER - XYLENE				
JL3080B	0.091	0.060	-0.031	-0.34
AU2782R	0.093	0.066	-0.027	-0.29
OC2782B	0.112	0.115	0.004	0.03
AU0183B	0.102	0.069	-0.033	-0.32
Group Average	0.099	0.078	-0.022	-0.23
S. Dev.	0.009	0.025	0.017	0.18
Avg. Abs. Value			0.024	0.24
S. Dev.			0.013	0.14

Table A-16

1,3,5-TRIMETHYL BENZENE - NOx - AIR RUNS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - MESITYLENE											
EC900	0.53	5.4	10.2	0.381	0.443	0.062	0.16	3.85	999.00		
EC901	0.51	2.7	5.2	0.384	0.413	0.029	0.08	8.88	8.54	-0.34	-0.04
EC903	1.00	4.7	4.7	0.502	0.565	0.063	0.12	14.96	14.04	-0.92	-0.06
Group Average	0.68	4.3	6.7	0.422	0.474	0.051	0.12	9.23	340.53	-0.63	-0.05
S. Dev.	0.28	1.4	3.1	0.069	0.080	0.019	0.04	5.56	570.26	0.41	0.02
Avg. Abs. Value						0.051	0.12			0.63	0.05
S. Dev.						0.019	0.04			0.41	0.02
2. SAPRC ITC - MESITYLENE											
ITC703	0.50	5.3	10.6	0.707	0.489	-0.218	-0.31	14.59	18.09	3.50	0.24
ITC706	0.49	2.7	5.4	0.641	0.476	-0.165	-0.26	7.20	8.57	1.36	0.19
ITC709	0.99	4.7	4.7	0.779	0.621	-0.158	-0.20	11.74	13.90	2.16	0.18
ITC742	0.48	4.6	9.7	0.773	0.489	-0.284	-0.37	13.14	14.56	1.42	0.11
ITC826	0.90	0.8	0.9	0.022	0.012	-0.009		1.68	2.33	0.65	0.39
Group Average	0.67	3.6	6.3	0.584	0.418	-0.167	-0.28	9.67	11.49	1.82	0.22
S. Dev.	0.25	1.9	3.9	0.320	0.234	0.101	0.07	5.26	6.15	1.08	0.10
Avg. Abs. Value						0.167	0.28			1.82	0.22
S. Dev.						0.101	0.07			1.08	0.10

Table A-16 (Continued)

Experiment	Half-Life 135-TMB				Maximum Concentration PAN			
	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - MESITYLENE								
EC900		45			0.400	0.193	-0.207	-0.52
EC901	47	42	-5	-0.11	0.293	0.174	-0.119	-0.41
EC903	49	45	-4	-0.08	0.470	0.331	-0.139	-0.30
Group Average	48	44	-4	-0.09	0.388	0.232	-0.155	-0.41
S. Dev.	1	1	0	0.02	0.089	0.085	0.046	0.11
Avg. Abs. Value			4	0.09			0.155	0.41
S. Dev.			0	0.02			0.046	0.11
2. SAPRC ITC - MESITYLENE								
ITC703	45	39	-6	-0.13	0.586	0.186	-0.400	-0.68
ITC706	45	38	-7	-0.16	0.440	0.180	-0.260	-0.59
ITC709	52	47	-5	-0.10	0.590	0.347	-0.243	-0.41
ITC742	42	40	-2	-0.05	0.470	0.181	-0.289	-0.62
ITC826	112	77	-35	-0.31	0.003	0.003	0.000	0.00
Group Average	59	48	-11	-0.15	0.418	0.179	-0.238	-0.46
S. Dev.	29	16	13	0.10	0.241	0.122	0.147	0.27
Avg. Abs. Value			11	0.15			0.238	0.46
S. Dev.			13	0.10			0.147	0.27

Table A-17

MIXTURES OF LIKE COMPOUNDS

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - Mixed Alkenes											
EC144	0.51	4.7	9.3	1.065	0.830	-0.235	-0.22	10.53	7.24	-3.29	-0.31
EC145	0.99	3.4	3.4	0.777	0.488	-0.289	-0.37	5.11	4.69	-0.42	-0.08
EC160	0.99	3.2	3.3	0.874	0.435	-0.440	-0.50	5.86	4.22	-1.64	-0.28
EC149	0.99	2.0	2.0	0.286	0.159	-0.127	-0.44	10.83	5.42	-5.41	-0.50
EC150	1.00	3.5	3.5	0.799	0.421	-0.378	-0.47	6.30	4.97	-1.33	-0.21
EC151	2.06	5.2	2.5	0.147	0.168	0.022	0.15	8.43	9.44	1.01	0.12
EC152	0.50	3.7	7.3	0.791	0.687	-0.105	-0.13	10.41	7.99	-2.43	-0.23
EC153	0.97	6.6	6.8	1.050	0.857	-0.193	-0.18	19.23	13.75	-5.47	-0.28
EC161	0.51	3.2	6.4	0.857	0.630	-0.227	-0.27	9.94	5.49	-4.45	-0.45
Group Average	0.95	4.0	5.0	0.738	0.519	-0.219	-0.27	9.63	7.02	-2.60	-0.25
S. Dev.	0.48	1.4	2.5	0.316	0.255	0.141	0.21	4.22	3.05	2.25	0.19
Avg. Abs. Value						0.224	0.30			2.83	0.27
S. Dev.						0.132	0.15			1.92	0.14
2. UNC CHAMBER - Mixed Alkenes											
OC1278R	0.48	1.4	3.0	0.260	0.263	0.003	0.01	1.14	1.28	0.14	0.13
OC2578R	0.44	1.4	3.1	0.147	0.137	-0.011	-0.07	0.94	1.04	0.10	0.11
AU0180R	0.56	0.5	0.8	0.256	0.056	-0.200	-0.78	0.98	0.53	-0.45	-0.46
AU1480R	0.47	1.4	3.0	0.863	0.394	-0.469	-0.54	2.13	1.32	-0.81	-0.38
Group Average	0.49	1.2	2.5	0.382	0.213	-0.169	-0.35	1.30	1.04	-0.25	-0.15
S. Dev.	0.05	0.5	1.1	0.325	0.148	0.220	0.38	0.56	0.36	0.46	0.31
Avg. Abs. Value						0.170	0.35			0.38	0.27
S. Dev.						0.219	0.37			0.33	0.18
3. SAPRC EC - Mixed Alkanes											
EC166	0.10	9.2	92.0	0.462	0.473	0.012	0.03	2.11	1.83	-0.28	-0.13
EC172	0.10	2.8	28.9	0.369	0.400	0.032	0.09	1.00	1.01	0.02	0.02
Group Average	0.10	6.0	60.5	0.415	0.437	0.022	0.06	1.55	1.42	-0.13	-0.06
S. Dev.	0.00	4.5	44.6	0.066	0.052	0.014	0.04	0.79	0.58	0.21	0.10
Avg. Abs. Value						0.022	0.06			0.15	0.07
S. Dev.						0.014	0.04			0.19	0.08

Table A-17 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
4. UNC CHAMBER - Mixed Aromatics											
ST0682R	0.46	2.8	6.2	0.378	0.306	-0.073	-0.19	1.11	1.09	-0.02	-0.01
ST0682B	0.45	2.9	6.5	0.478	0.450	-0.027	-0.06	1.35	1.34	-0.02	-0.01
Group Average	0.46	2.9	6.3	0.428	0.378	-0.050	-0.12	1.23	1.22	-0.02	-0.01
S. Dev.	0.01	0.1	0.2	0.070	0.102	0.032	0.09	0.17	0.17	0.00	0.00
Avg. Abs. Value						0.050	0.12			0.02	0.01
S. Dev.						0.032	0.09			0.00	0.00

Table A-17 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - Mixed Alkenes								
EC144	0.075	0.062	-0.013	-0.17	0.846	0.824	-0.022	-0.03
EC145	0.112	0.080	-0.032	-0.28	0.516	0.577	0.062	0.12
EC160	0.158	0.068	-0.089	-0.57	0.500	0.550	0.050	0.10
EC149	0.112	0.063	-0.048	-0.43	0.105	0.246	0.141	1.35
EC150	0.145	0.073	-0.072	-0.50	0.433	0.524	0.091	0.21
EC151	0.077	0.069	-0.009	-0.11	0.512	0.655	0.144	0.28
EC152	0.115	0.101	-0.014	-0.12	0.262	0.527	0.265	1.01
EC153	0.175	0.151	-0.023	-0.13	0.645	0.945	0.301	0.47
EC161	0.125	0.086	-0.039	-0.31	0.423	0.475	0.052	0.12
Group Average	0.121	0.084	-0.038	-0.29	0.471	0.591	0.120	0.40
S. Dev.	0.034	0.028	0.028	0.17	0.211	0.202	0.105	0.47
Avg. Abs. Value			0.038	0.29			0.125	0.41
S. Dev.			0.028	0.17			0.098	0.46
2. UNC CHAMBER - Mixed Alkenes								
OC1278R	0.053	0.091	0.038	0.73				
OC2578R	0.041	0.070	0.030	0.73				
AU0180R	0.013	0.002	-0.011	-0.87	0.230	0.065	-0.165	-0.72
AU1480R	0.058	0.019	-0.038	-0.67	0.402	0.169	-0.233	-0.58
Group Average	0.041	0.046	0.005	-0.02	0.316	0.117	-0.199	-0.65
S. Dev.	0.020	0.042	0.036	0.87	0.122	0.073	0.048	0.10
Avg. Abs. Value			0.029	0.75			0.199	0.65
S. Dev.			0.013	0.09			0.048	0.10
3. SAPRC EC - Mixed Alkanes								
EC166	0.040	0.037	-0.003	-0.07	0.010	0.013	0.003	0.30
EC172	0.029	0.032	0.003	0.10	0.010	0.011	0.001	0.05
Group Average	0.034	0.035	0.000	0.02	0.010	0.012	0.002	0.18
S. Dev.	0.008	0.004	0.004	0.12	0.000	0.002	0.002	0.17
Avg. Abs. Value			0.003	0.08			0.002	0.18
S. Dev.			0.000	0.02			0.002	0.17

Table A-17 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
4. UNC CHAMBER - Mixed Aromatics								
ST0682R	0.043	0.031	-0.011	-0.27	0.088	0.024	-0.064	-0.73
ST0682B	0.061	0.060	-0.001	-0.02	0.100	0.029	-0.071	-0.71
Group Average	0.052	0.045	-0.006	-0.15	0.094	0.027	-0.067	-0.72
S. Dev.	0.013	0.020	0.007	0.18	0.008	0.004	0.005	0.01
Avg. Abs. Value			0.006	0.15			0.067	0.72
S. Dev.			0.007	0.18			0.005	0.01

Table A-18

MISCELLANEOUS SIMPLE (NON-SURROGATE) MIXTURES

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - ALKANE/OLEFIN											
EC106	0.50	9.2	18.3	0.592	0.685	0.093	0.16	3.80	4.26	0.45	0.12
EC113	0.11	9.5	85.0	0.352	0.465	0.113	0.32	5.26	6.52	1.26	0.24
EC114	1.00	17.3	17.3	0.744	0.802	0.057	0.08	8.03	6.90	-1.13	-0.14
EC115	0.51	12.7	25.2	0.590	0.702	0.112	0.19	3.78	3.72	-0.06	-0.02
EC116	0.49	18.6	37.6	0.743	0.815	0.072	0.10	8.28	9.27	0.98	0.12
Group Average	0.52	13.5	36.7	0.604	0.694	0.090	0.17	5.83	6.13	0.30	0.06
S. Dev.	0.31	4.3	28.2	0.160	0.140	0.025	0.10	2.21	2.23	0.95	0.15
Avg. Abs. Value						0.090	0.17			0.78	0.13
S. Dev.						0.025	0.10			0.51	0.08
2. UNC CHAMBER - ALKANE/OLEFIN											
JL1581R	0.27	2.3	8.4	0.485	0.453	-0.032	-0.07	1.08	0.96	-0.12	-0.11
JL1881R	0.26	2.1	8.0	0.658	0.395	-0.263	-0.40	1.31	1.00	-0.30	-0.23
ST2481R	0.23	1.6	6.7	0.211	0.300	0.089	0.42	0.62	0.83	0.21	0.34
AU2781R	0.23	2.1	9.2	0.554	0.521	-0.033	-0.06	0.95	1.03	0.08	0.08
OC0382R	0.25	2.7	11.0	0.247	0.442	0.195	0.79	0.76	0.90	0.14	0.18
OC0382B	0.25	1.9	7.7	0.158	0.272	0.114	0.72	0.62	0.72	0.10	0.17
NV1582R	0.18	2.6	14.4	0.061	0.179	0.118	1.95	0.42	0.57	0.15	0.35
Group Average	0.24	2.2	9.3	0.339	0.366	0.027	0.48	0.82	0.86	0.04	0.11
S. Dev.	0.03	0.4	2.6	0.225	0.120	0.152	0.78	0.31	0.17	0.18	0.22
Avg. Abs. Value						0.121	0.63			0.16	0.21
S. Dev.						0.084	0.65			0.08	0.11
3. UNC CHAMBER - UNC MIX											
JL2281R	0.26	2.4	9.1	0.626	0.409	-0.217	-0.35	1.18	0.94	-0.24	-0.20
JL2181B	0.24	1.3	5.4	0.237	0.249	0.012	0.05	0.63	0.67	0.04	0.06
NV1582B	0.18	2.7	14.9	0.167	0.286	0.119	0.72	0.71	1.03	0.32	0.45
DE0782B	0.19	3.5	18.7	0.093	0.306	0.214	2.31	0.55	1.16	0.61	1.12
Group Average	0.22	2.5	12.0	0.281	0.313	0.032	0.68	0.77	0.95	0.18	0.36
S. Dev.	0.04	0.9	5.9	0.238	0.069	0.185	1.17	0.28	0.21	0.36	0.57
Avg. Abs. Value						0.140	0.86			0.30	0.46
S. Dev.						0.097	1.01			0.24	0.47

Table A-18 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
4. SAPRC EC - OLEFIN/AROMATIC											
EC335	0.44	7.7	17.4	0.398	0.462	0.063	0.16	4.64	4.56	-0.09	-0.02
EC329	0.45	4.2	9.2	0.403	0.433	0.029	0.07	3.27	3.18	-0.09	-0.03
EC330	0.29	4.3	14.6	0.344	0.390	0.046	0.13	3.91	3.53	-0.38	-0.10
EC334	0.45	8.1	18.2	0.408	0.465	0.057	0.14	5.59	5.08	-0.51	-0.09
EC338	0.45	15.0	33.7	0.484	0.612	0.128	0.27	5.19	4.87	-0.32	-0.06
Group Average	0.42	7.9	18.6	0.407	0.472	0.065	0.15	4.52	4.24	-0.28	-0.06
S. Dev.	0.07	4.4	9.1	0.050	0.084	0.038	0.07	0.94	0.84	0.18	0.04
Avg. Abs. Value						0.065	0.15			0.28	0.06
S. Dev.						0.038	0.07			0.18	0.04
5. UNC CHAMBER - OLEFIN/AROMATIC											
JN1379B	0.44	6.1	13.7	0.756	0.757	0.002	0.00	2.44	2.98	0.54	0.22
Group Average	0.44	6.1	13.7	0.756	0.757	0.002	0.00	2.44	2.98	0.54	0.22
S. Dev.											
Avg. Abs. Value						0.002	0.00			0.54	0.22
S. Dev.											
6. SAPRC EC - ALKANE/AROMATIC											
EC328	0.45	12.1	27.1	0.523	0.584	0.061	0.12	3.50	3.43	-0.07	-0.02
Group Average	0.45	12.1	27.1	0.523	0.584	0.061	0.12	3.50	3.43	-0.07	-0.02
S. Dev.											
Avg. Abs. Value						0.061	0.12			0.07	0.02
S. Dev.											

Table A-18

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO				Half-Life PROPENE			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
1. SAPRC EC - ALKANE/OLEFIN												
EC106	0.162	0.178	0.016	0.10	0.207	0.187	-0.021	-0.10	134	133	-1	-0.01
EC113	0.060	0.084	0.024	0.40		0.176			82	78	-4	-0.05
EC114	0.231	0.241	0.010	0.05	0.433	0.361	-0.072	-0.17	112	145	33	0.29
EC115	0.134	0.152	0.019	0.14	0.201	0.149	-0.052	-0.26	130	151	21	0.16
EC116	0.186	0.202	0.016	0.09	0.463	0.386	-0.078	-0.17	90	91	1	0.01
Group Average	0.155	0.172	0.017	0.15	0.326	0.252	-0.056	-0.17	109	119	10	0.08
S. Dev.	0.064	0.059	0.005	0.14	0.141	0.112	0.026	0.06	23	33	16	0.14
Avg. Abs. Value			0.017	0.15			0.056	0.17			12	0.10
S. Dev.			0.005	0.14			0.026	0.06			14	0.12
2. UNC CHAMBER - ALKANE/OLEFIN												
JL1581R	0.097	0.055	-0.043	-0.44	0.157	0.087	-0.071	-0.45	248	292	44	0.18
JL1881R	0.046	0.054	0.008	0.18	0.080	0.073	-0.007	-0.09	258	275	17	0.07
ST2481R		0.048			0.224	0.065	-0.159	-0.71	312	249	-63	-0.20
AU2781R		0.040			0.164	0.086	-0.078	-0.48	250	250	0	0.00
OC0382R	0.008	0.028	0.020	2.58		0.124				267		
OC0382B	0.004	0.013	0.009	2.57		0.080				255		
NV1582R	0.004	0.006	0.002	0.35	0.090	0.063	-0.027	-0.30	435	253	-182	-0.42
Group Average	0.032	0.035	-0.001	1.05	0.143	0.083	-0.068	-0.40	300	263	-36	-0.08
S. Dev.	0.041	0.020	0.024	1.42	0.059	0.021	0.059	0.23	79	15	90	0.24
Avg. Abs. Value			0.016	1.22			0.068	0.40			61	0.17
S. Dev.			0.016	1.24			0.059	0.23			71	0.16
3. UNC CHAMBER - UNC MIX												
JL2281R	0.055	0.023	-0.032	-0.58	0.174	0.058	-0.116	-0.66				
JL2181B	0.013	0.015	0.003	0.21		0.051						
NV1582B	0.008	0.033	0.024	2.87	0.150	0.085	-0.065	-0.44				
DE0782B	0.009	0.036	0.027	3.20	0.100	0.101	0.001	0.01				
Group Average	0.021	0.027	0.006	1.42	0.141	0.074	-0.060	-0.36				
S. Dev.	0.023	0.009	0.027	1.89	0.038	0.023	0.058	0.34				
Avg. Abs. Value			0.022	1.71			0.061	0.37				
S. Dev.			0.013	1.54			0.057	0.33				

Table A-18

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO				Half-Life PROPENE			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
4. SAPRC EC - OLEFIN/AROMATIC												
EC335	0.115	0.147	0.033	0.28	0.117	0.070	-0.047	-0.40				
EC329	0.067	0.082	0.015	0.23	0.088	0.071	-0.017	-0.19	73	95	22	0.30
EC330	0.058	0.074	0.016	0.27	0.098	0.063	-0.035	-0.35	59	81	22	0.37
EC334	0.071	0.100	0.029	0.40	0.113	0.074	-0.039	-0.35	63	86	23	0.37
EC338	0.076	0.110	0.034	0.44	0.091	0.034	-0.057	-0.62				
Group Average	0.077	0.103	0.025	0.33	0.101	0.062	-0.039	-0.38	65	87	22	0.35
S. Dev.	0.022	0.029	0.009	0.09	0.013	0.016	0.015	0.15	7	7	0	0.04
Avg. Abs. Value			0.025	0.33			0.039	0.38			22	0.35
S. Dev.			0.009	0.09			0.015	0.15			0	0.04
5. UNC CHAMBER - OLEFIN/AROMATIC												
JN1379B	0.181	0.222	0.041	0.23	0.340	0.381	0.041	0.12	249	209	-40	-0.16
Group Average	0.181	0.222	0.041	0.23	0.340	0.381	0.041	0.12	249	209	-40	-0.16
S. Dev.												
Avg. Abs. Value			0.041	0.23			0.041	0.12			40	0.16
S. Dev.												
6. Runs IDs = EC ALKARO												
EC328	0.074	0.087	0.013	0.18	0.088	0.029	-0.059	-0.67				
Group Average	0.074	0.087	0.013	0.18	0.088	0.029	-0.059	-0.67				
S. Dev.												
Avg. Abs. Value			0.013	0.18			0.059	0.67				
S. Dev.												

Table A-19

MINIMUM SURROGATE MIXTURES

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC ITC - MINI SURROGATE											
ITC479	0.09	4.0	43.4	0.332	0.356	0.024	0.07	2.95	4.59	1.64	0.56
ITC584	0.10	4.0	40.7	0.375	0.348	-0.027	-0.07	3.05	3.74	0.69	0.23
ITC579	0.10	3.4	34.7	0.356	0.332	-0.025	-0.07	1.54	2.19	0.65	0.43
ITC472	0.10	3.6	35.1	0.258	0.363	0.105	0.41	1.72	2.96	1.25	0.73
ITC474	0.09	4.2	45.1	0.293	0.362	0.069	0.24	3.40	5.71	2.31	0.68
ITC581	0.09	4.3	50.0	0.352	0.338	-0.015	-0.04	3.74	5.01	1.27	0.34
ITC585	0.10	4.8	50.8	0.311	0.333	0.022	0.07	5.11	6.64	1.54	0.30
ITC478	0.10	5.0	52.6	0.320	0.351	0.031	0.10	4.73	7.86	3.14	0.66
ITC482	0.10	1.2	12.3	0.279	0.320	0.041	0.15	2.44	4.17	1.73	0.71
ITC488	0.09	6.0	66.2	0.293	0.369	0.076	0.26	3.06	4.89	1.83	0.60
ITC492	0.09	8.1	88.4	0.326	0.395	0.069	0.21	3.28	5.06	1.78	0.54
ITC494	0.09	8.5	92.5	0.321	0.401	0.080	0.25	3.30	5.00	1.69	0.51
ITC498	0.10	3.9	40.2	0.320	0.369	0.049	0.15	2.16	3.44	1.28	0.59
ITC500	0.10	4.1	42.7	0.286	0.352	0.065	0.23	5.18	7.13	1.95	0.38
ITC502	0.09	4.6	49.5	0.271	0.331	0.061	0.22	7.07	12.43	5.36	0.76
ITC462	0.11	7.5	71.3	0.099	0.202	0.103	1.04	0.70	0.76	0.06	0.09
ITC466	0.10	6.5	62.7	0.131	0.225	0.094	0.72	0.77	1.04	0.28	0.36
ITC468	0.09	4.6	49.0	0.176	0.276	0.100	0.57	1.19	2.07	0.88	0.74
ITC451	0.10	5.2	52.0	0.312	0.341	0.029	0.09	3.95	5.46	1.51	0.38
ITC455	0.09	4.4	47.8	0.304	0.342	0.039	0.13	3.52	4.87	1.35	0.38
ITC977	0.13	3.2	25.1	0.329	0.358	0.028	0.09	3.94	3.35	-0.59	-0.15
ITC985	0.12	2.7	22.9	0.336	0.329	-0.007	-0.02	3.95	3.20	-0.75	-0.19
ITC997	0.12	2.7	23.0	0.316	0.325	0.009	0.03	3.89	3.14	-0.74	-0.19
ITC979	0.12	2.9	23.1	0.404	0.445	0.041	0.10	4.88	4.09	-0.79	-0.16
ITC992	0.12	2.6	20.9	0.384	0.429	0.045	0.12	5.57	4.56	-1.01	-0.18
Group Average	0.10	4.5	45.7	0.299	0.344	0.044	0.20	3.40	4.53	1.13	0.36
S. Dev.	0.01	1.8	19.9	0.072	0.053	0.039	0.25	1.55	2.38	1.40	0.32
Avg. Abs. Value						0.050	0.22			1.44	0.43
S. Dev.						0.030	0.24			1.06	0.21

Table A-19 (Continued)

Experiment	Initial Concentrations NOx (ppm)	Initial Concentrations HC (ppmC)	Initial Concentrations HC/NOx	Maximum Concentration OZONE Expt (ppm)	Maximum Concentration OZONE Calc (ppm)	Maximum Concentration OZONE Calc -Expt (ppm)	Maximum Concentration OZONE Calc -Expt /Expt	Average Initial d([O3] - [NO])/dt Expt --	Average Initial d([O3] - [NO])/dt Calc (ppb/min)	Average Initial d([O3] - [NO])/dt Calc -Expt --	Average Initial d([O3] - [NO])/dt Calc -Expt /Expt
2. UNC CHAMBER - PBA SURROGATE											
JL1581B	0.28	2.3	8.0	0.474	0.389	-0.085	-0.18	1.10	0.89	-0.21	-0.19
ST2481B	0.23	1.9	8.1	0.246	0.302	0.056	0.23	0.71	0.84	0.14	0.19
JN0982B	0.28	3.1	11.0	0.667	0.455	-0.212	-0.32	1.37	1.15	-0.22	-0.16
JN1483R	0.22	2.6	11.6	0.585	0.526	-0.059	-0.10	1.10	1.13	0.03	0.02
JN2783B	0.26	2.9	11.1	0.511	0.520	0.009	0.02	1.01	1.05	0.04	0.04
AU1883B	0.28	0.6	2.0	0.556	0.383	-0.173	-0.31	0.70	0.57	-0.13	-0.18
AU2683R	0.32	2.6	8.1	0.646	0.437	-0.209	-0.32	1.24	1.02	-0.23	-0.18
JL1881B	0.27	2.3	8.5	0.693	0.525	-0.168	-0.24	1.91	1.55	-0.36	-0.19
JN0982R	0.29	3.1	10.7	0.714	0.542	-0.173	-0.24	1.77	1.50	-0.27	-0.15
Group Average	0.27	2.4	8.8	0.566	0.453	-0.112	-0.16	1.21	1.08	-0.13	-0.09
S. Dev.	0.03	0.8	2.9	0.145	0.083	0.098	0.18	0.42	0.31	0.17	0.14
Avg. Abs. Value						0.127	0.22			0.18	0.15
S. Dev.						0.075	0.10			0.11	0.07

Table A-19 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO				Half-Life PROPENE			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
1. SAPRC ITC - MINI SURROGATE												
ITC479	0.050	0.047	-0.003	-0.07		0.057			84	84	0	0.00
ITC584	0.080	0.049	-0.031	-0.39		0.051			98	96	-2	-0.02
ITC579	0.058	0.040	-0.018	-0.31		0.007						
ITC472	0.044	0.042	-0.002	-0.04		0.008						
ITC474	0.051	0.051	0.000	0.00		0.092			90	81	-9	-0.10
ITC581	0.090	0.049	-0.041	-0.45		0.088			94	89	-5	-0.05
ITC585	0.066	0.054	-0.012	-0.18		0.137			91	87	-4	-0.04
ITC478	0.056	0.055	-0.001	-0.01		0.155			80	79	-1	-0.01
ITC482	0.052	0.051	-0.001	-0.02		0.063			80	75	-5	-0.06
ITC488	0.051	0.044	-0.007	-0.13		0.055			90	88	-2	-0.02
ITC492	0.054	0.045	-0.009	-0.18		0.054			89	92	3	0.03
ITC494	0.053	0.045	-0.008	-0.15		0.053			92	94	2	0.02
ITC498	0.048	0.046	-0.002	-0.04		0.047			101	96	-5	-0.05
ITC500	0.060	0.054	-0.006	-0.10		0.069			62	73	11	0.18
ITC502	0.066	0.060	-0.006	-0.10		0.082			64	74	10	0.16
ITC462	0.004	0.016	0.012	3.01		0.008			329	258	-71	-0.22
ITC466	0.007	0.021	0.014	1.93		0.010			280	219	-61	-0.22
ITC468	0.021	0.030	0.009	0.44		0.028			160	136	-24	-0.15
ITC451	0.048	0.044	-0.004	-0.09		0.062			70	77	7	0.10
ITC455	0.050	0.043	-0.007	-0.14		0.058			79	80	1	0.01
ITC977	0.035	0.053	0.018	0.52		0.046			80	97	17	0.21
ITC985	0.036	0.045	0.009	0.25		0.042			75	92	17	0.23
ITC997	0.038	0.045	0.007	0.17		0.041			68	93	25	0.37
ITC979	0.027	0.056	0.028	1.04		0.037			89	106	17	0.19
ITC992	0.041	0.049	0.008	0.18		0.031			75	106	31	0.41
Group Average	0.047	0.045	-0.002	0.21					105	103	-2	0.04
S. Dev.	0.019	0.010	0.015	0.76					66	45	23	0.17
Avg. Abs. Value			0.011	0.40							14	0.12
S. Dev.			0.010	0.68							18	0.11

Table A-19 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO				Half-Life PROPENE			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
2. UNC CHAMBER - PBA SURROGATE												
JL1581B	0.079	0.045	-0.034	-0.43	0.166	0.069	-0.098	-0.59	243	295	52	0.21
ST2481B		0.043			0.190	0.049	-0.141	-0.74	278	236	-42	-0.15
JN0982B		0.080				0.080			295	270	-25	-0.08
JN1483R	0.063	0.073	0.010	0.16	0.054	0.070	0.017	0.31	281	253	-28	-0.10
JN2783B	0.065	0.066	0.001	0.01	0.105	0.074	-0.031	-0.29	295	273	-22	-0.07
AU1883B	0.055	0.033	-0.022	-0.40	0.120	0.056	-0.065	-0.54	285	309	24	0.08
AU2683R		0.051			0.141	0.067	-0.074	-0.53	209	278	69	0.33
JL1881B	0.061	0.098	0.037	0.61	0.150	0.076	-0.075	-0.50	196	208	12	0.06
JN0982R		0.129				0.092			245	235	-10	-0.04
Group Average	0.064	0.069	-0.002	-0.01	0.132	0.070	-0.067	-0.41	258	261	3	0.03
S. Dev.	0.009	0.031	0.028	0.43	0.045	0.013	0.050	0.34	37	31	38	0.16
Avg. Abs. Value			0.021	0.32			0.071	0.50			31	0.13
S. Dev.			0.015	0.24			0.041	0.16			19	0.09

Table A-20

RUNS USING COMPLEX SURROGATE MIXTURES

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
1. SAPRC EC - 7 HYDROCARBON SURROGATE											
EC231	0.49	13.2	26.9	0.620	0.788	0.168	0.27	6.99	8.74	1.75	0.25
EC232	0.49	9.3	18.9	0.342	0.526	0.184	0.54	3.12	3.37	0.24	0.08
EC233	0.10	9.5	92.5	0.330	0.463	0.133	0.40	4.07	5.25	1.18	0.29
EC237	0.48	10.5	21.6	0.652	0.716	0.064	0.10	7.36	6.80	-0.56	-0.08
EC238	0.95	10.1	10.6	0.691	0.791	0.100	0.14	5.10	5.73	0.64	0.12
EC241	0.49	5.0	10.2	0.408	0.463	0.055	0.13	2.87	3.28	0.42	0.15
EC242	0.50	12.9	25.6	0.682	0.716	0.034	0.05	17.53	18.50	0.96	0.06
EC243	0.50	9.7	19.5	0.716	0.752	0.036	0.05	14.50	13.86	-0.65	-0.04
EC245	1.00	12.9	12.9	0.894	0.906	0.012	0.01	13.41	14.66	1.24	0.09
EC246	0.51	8.6	17.0	0.574	0.601	0.027	0.05	2.65	2.53	-0.12	-0.05
EC247	0.51	6.2	12.2	0.657	0.666	0.009	0.01	7.49	6.93	-0.56	-0.08
Group Average	0.55	9.8	24.4	0.597	0.672	0.075	0.16	7.74	8.15	0.41	0.07
S. Dev.	0.24	2.6	23.3	0.173	0.144	0.062	0.17	5.16	5.27	0.82	0.13
Avg. Abs. Value						0.075	0.16			0.76	0.12
S. Dev.						0.062	0.17			0.48	0.08
2. SAPRC ITC - SAI SURROGATE											
ITC626	0.30	4.0	13.4	0.618	0.614	-0.004	-0.01	2.18	2.67	0.49	0.23
ITC630	0.31	1.9	6.3	0.284	0.276	-0.007	-0.03	0.86	1.12	0.26	0.30
ITC631	0.32	1.0	3.2	0.043	0.050	0.008		0.47	0.56	0.09	0.20
ITC633	0.64	4.0	6.2	0.231	0.287	0.056	0.24	1.26	1.83	0.57	0.45
ITC635	1.21	4.0	3.3	0.006	0.017	0.011		0.95	1.30	0.34	0.36
ITC637	0.31	4.0	12.8	0.617	0.610	-0.007	-0.01	2.31	2.64	0.33	0.14
ITC865	0.28	8.4	29.9	0.632	0.599	-0.033	-0.05	2.60	4.26	1.66	0.64
ITC867	0.28	4.8	17.2	0.631	0.619	-0.012	-0.02	2.23	4.32	2.09	0.94
ITC868	0.37	2.9	7.8	0.518	0.459	-0.059	-0.11	2.10	1.64	-0.46	-0.22
ITC871	0.37	1.7	4.6	0.376	0.257	-0.118	-0.32	1.18	1.22	0.04	0.03
ITC872	0.38	2.1	5.7	0.213	0.219	0.006	0.03	1.20	1.50	0.30	0.25
ITC873	0.39	1.3	3.4	0.160	0.097	-0.063	-0.39	0.85	0.84	0.00	-0.01
ITC874	0.38	2.1	5.7	0.191	0.147	-0.043	-0.23	0.83	0.94	0.11	0.13
ITC877	0.38	2.3	6.2	0.250	0.229	-0.021	-0.08	1.14	1.48	0.34	0.30
ITC880	0.73	2.2	3.0	0.031	0.035	0.004		0.85	1.10	0.25	0.29
ITC881	0.73	2.3	3.1	0.012	0.023	0.011		1.03	1.19	0.16	0.15
ITC885	0.64	1.5	2.4	0.012	0.020	0.009		0.44	0.83	0.40	0.91
ITC886	0.73	2.3	3.1	0.012	0.017	0.006		1.24	0.75	-0.50	-0.40
ITC888	0.33	4.7	14.5	0.579	0.575	-0.004	-0.01	1.65	2.26	0.61	0.37
ITC891	0.32	4.4	13.7	0.602	0.584	-0.018	-0.03	2.67	3.50	0.83	0.31
Group Average	0.47	3.1	8.3	0.301	0.287	-0.014	-0.07	1.40	1.80	0.40	0.27
S. Dev.	0.24	1.7	6.8	0.248	0.240	0.036	0.16	0.70	1.13	0.60	0.32
Avg. Abs. Value						0.025	0.11			0.49	0.33
S. Dev.						0.030	0.13			0.52	0.25

Table A-20 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
3. SAPRC OTC - SAI SURROGATE											
OTC189A	0.45	3.3	7.4	0.576	0.645	0.070	0.12	3.79	3.55	-0.24	-0.06
OTC189B	0.45	4.0	8.9	0.712	0.719	0.007	0.01	3.70	3.58	-0.11	-0.03
OTC190A	0.41	3.8	9.2	0.702	0.724	0.022	0.03	4.24	3.19	-1.05	-0.25
OTC190B	0.42	3.8	9.0	0.669	0.675	0.006	0.01	3.73	2.81	-0.92	-0.25
OTC192A	0.47	4.2	8.9	0.735	0.735	0.000	0.00	4.25	3.29	-0.96	-0.23
OTC192B	0.47	4.2	8.9	0.754	0.617	-0.137	-0.18	3.84	2.67	-1.17	-0.30
OTC194A	0.38	7.4	19.3	0.737	1.014	0.276	0.37	7.85	8.62	0.77	0.10
OTC194B	0.38	3.7	9.7	0.603	0.616	0.013	0.02	2.95	3.01	0.06	0.02
OTC195A	0.41	1.8	4.5	0.164	0.086	-0.078	-0.47	2.05	1.12	-0.93	-0.45
OTC195B	0.41	4.1	9.9	0.681	0.667	-0.014	-0.02	4.14	3.68	-0.46	-0.11
OTC196B	0.41	3.7	9.1	0.597	0.666	0.068	0.11	3.86	3.22	-0.64	-0.17
OTC197A	0.38	3.6	9.5	0.621	0.484	-0.137	-0.22	4.12	2.60	-1.51	-0.37
OTC197B	0.77	3.1	4.1	0.152	0.070	-0.082	-0.54	2.86	2.06	-0.80	-0.28
OTC198A	0.84	5.4	6.4	0.704	0.509	-0.195	-0.28	6.09	4.20	-1.89	-0.31
OTC198B	0.40	3.7	9.4	0.674	0.544	-0.130	-0.19	3.86	2.42	-1.44	-0.37
OTC199A	0.36	3.5	9.6	0.591	0.562	-0.029	-0.05	3.86	2.97	-0.89	-0.23
OTC199B	0.37	3.5	9.6	0.606	0.549	-0.057	-0.09	3.40	2.85	-0.55	-0.16
OTC202A	0.73	6.0	8.2	0.714	0.402	-0.313	-0.44	6.95	16.10	9.15	1.32
OTC202B	0.40	2.6	6.7	0.522	0.341	-0.181	-0.35	3.82	3.00	-0.81	-0.21
OTC203A	0.39	3.5	9.0	0.231	0.241	0.010	0.04	2.34	2.37	0.03	0.01
OTC203B	0.19	3.5	18.5	0.394	0.496	0.102	0.26	2.20	2.73	0.53	0.24
OTC204A	0.35	3.6	10.2	0.302	0.331	0.029	0.10	3.27	3.58	0.31	0.10
OTC204B	0.17	3.5	20.3	0.381	0.511	0.130	0.34	2.62	2.99	0.37	0.14
OTC205A	0.84	3.8	4.5	0.039	0.045	0.006		4.85	2.11	-2.74	-0.57
OTC205B	0.14	3.6	26.5	0.392	0.579	0.187	0.48	4.49	3.76	-0.73	-0.16
OTC215A	0.45	3.5	7.8	0.830	0.831	0.001	0.00	4.33	3.66	-0.68	-0.16
OTC215B	0.44	4.1	9.3	0.868	0.965	0.097	0.11	5.33	5.72	0.39	0.07
OTC217A	0.50	4.9	9.6	0.483	0.501	0.018	0.04	2.55	2.53	-0.02	-0.01
OTC217B	0.51	4.6	9.0	0.831	0.883	0.051	0.06	4.64	4.21	-0.43	-0.09
OTC221A	0.41	2.4	5.8	0.235	0.221	-0.014	-0.06	1.63	1.45	-0.17	-0.11
OTC221B	0.42	2.0	4.7	0.333	0.282	-0.051	-0.15	1.63	1.58	-0.05	-0.03
OTC222A	0.44	3.4	7.8	0.909	0.813	-0.096	-0.11	3.83	3.41	-0.42	-0.11
OTC222B	0.43	2.6	6.0	0.940	1.023	0.083	0.09	5.55	5.79	0.23	0.04
OTC223A	0.36	4.8	13.4	0.953	0.832	-0.121	-0.13	4.55	3.88	-0.67	-0.15
OTC223B	0.40	3.5	8.8	0.771	0.604	-0.168	-0.22	3.15	2.60	-0.55	-0.17
OTC224A	0.34	4.4	12.7	0.776	0.737	-0.039	-0.05	3.67	2.83	-0.84	-0.23
OTC224B	0.34	4.3	12.6	0.813	0.855	0.042	0.05	4.94	4.45	-0.49	-0.10
OTC226A	0.45	2.5	5.5	0.751	0.405	-0.346	-0.46	3.12	2.11	-1.01	-0.32
OTC228A	0.41	2.4	6.0	0.246	0.321	0.075	0.31	1.49	1.86	0.37	0.25
OTC228B	0.41	2.3	5.6	0.296	0.361	0.065	0.22	1.79	2.49	0.71	0.39
OTC229A	0.46	3.0	6.6	0.253	0.359	0.106	0.42	1.56	1.94	0.38	0.25
OTC229B	0.46	1.7	3.8	0.168	0.297	0.129	0.77	1.38	1.80	0.42	0.31

Table A-20 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
OTC230A	0.41	3.1	7.6	0.489	0.738	0.249	0.51	2.43	2.98	0.55	0.23
OTC230B	0.41	1.7	4.2	0.271	0.431	0.160	0.59	1.66	2.10	0.45	0.27
OTC237A	0.52	4.3	8.2	0.807	0.718	-0.089	-0.11	4.10	3.39	-0.71	-0.17
OTC237B	0.52	4.4	8.5	0.757	0.585	-0.172	-0.23	3.48	2.89	-0.58	-0.17
OTC238A	0.50	2.9	5.8	0.406	0.319	-0.087	-0.21	2.58	2.20	-0.38	-0.15
OTC238B	0.50	3.9	7.8	0.702	0.618	-0.084	-0.12	4.06	3.55	-0.51	-0.13
OTC239A	0.49	2.7	5.4	0.343	0.304	-0.039	-0.11	2.66	2.42	-0.24	-0.09
OTC239B	0.50	2.5	5.0	0.234	0.120	-0.114	-0.49	1.85	1.43	-0.41	-0.22
OTC240A	0.50	1.8	3.6	0.034	0.027	-0.007		1.08	0.89	-0.20	-0.18
OTC240B	0.50	2.0	4.1	0.217	0.081	-0.136	-0.63	1.79	1.31	-0.48	-0.27
OTC241A	0.32	4.7	14.8	0.671	0.684	0.013	0.02	3.26	2.98	-0.28	-0.09
OTC241B	0.31	4.0	12.9	0.674	0.654	-0.020	-0.03	3.30	3.25	-0.05	-0.02
OTC242A	0.45	2.6	5.8	0.182	0.111	-0.071	-0.39	1.47	1.28	-0.19	-0.13
OTC242B	0.46	2.1	4.7	0.639	0.499	-0.140	-0.22	3.04	2.54	-0.50	-0.16
OTC243A	0.47	4.7	10.0	0.142	0.186	0.044	0.31	1.41	1.96	0.55	0.39
OTC243B	0.38	3.7	9.7	0.152	0.151	-0.001	0.00	1.40	2.20	0.80	0.57
OTC248A	0.48	3.7	7.7	0.056	0.051	-0.005	-0.08	1.40	1.25	-0.15	-0.11
OTC248B	0.46	2.9	6.3	0.081	0.073	-0.008	-0.10	1.61	1.70	0.08	0.05
OTC249A	0.48	5.6	11.8	0.348	0.279	-0.069	-0.20	2.55	2.36	-0.19	-0.07
OTC249B	0.46	4.9	10.7	0.325	0.321	-0.004	-0.01	2.83	3.01	0.18	0.06
Group Average	0.44	3.6	8.8	0.504	0.485	-0.019	-0.03	3.26	3.07	-0.19	-0.05
S. Dev.	0.12	1.1	4.2	0.263	0.265	0.115	0.28	1.42	2.08	1.37	0.28
Avg. Abs. Value						0.085	0.21			0.72	0.21
S. Dev.						0.079	0.19			1.18	0.19
4. UNC CHAMBER - UNC MIXTURES											
ST2081R	0.23	2.3	10.0	0.403	0.451	0.048	0.12	0.95	1.15	0.19	0.20
DE0782R	0.19	3.4	18.3	0.076	0.377	0.301	3.94	0.52	1.14	0.62	1.19
AU2681R	0.24	2.0	8.4	0.506	0.497	-0.009	-0.02	1.18	1.17	-0.01	-0.01
AU2681B	0.24	2.0	8.5	0.544	0.441	-0.103	-0.19	1.22	1.10	-0.12	-0.10
AU2781B	0.23	2.0	8.8	0.623	0.495	-0.128	-0.21	1.27	1.17	-0.10	-0.08
ST0381R	0.24	1.8	7.6	0.541	0.405	-0.137	-0.25	1.48	1.15	-0.33	-0.22
ST1081R	0.25	2.8	11.3	0.610	0.603	-0.008	-0.01	1.59	1.72	0.13	0.08
ST2081B	0.23	2.1	9.2	0.414	0.407	-0.007	-0.02	1.06	1.08	0.03	0.02
JL2081B	0.42	1.8	4.3	0.165	0.057	-0.108	-0.66	0.82	0.65	-0.17	-0.21
ST1682R	0.43	3.2	7.5	0.410	0.356	-0.053	-0.13	1.28	1.14	-0.14	-0.11
JL2081R	0.41	2.7	6.6	0.635	0.269	-0.367	-0.58	1.55	1.01	-0.54	-0.35
JL2281B	0.26	2.9	11.2	0.722	0.527	-0.195	-0.27	1.80	1.56	-0.24	-0.14
OC1481R	0.28	3.3	11.9	0.462	0.512	0.051	0.11	1.53	1.42	-0.11	-0.07
ST1682B	0.43	3.1	7.2	0.840	0.717	-0.123	-0.15	2.39	2.00	-0.39	-0.16
ST2981R	0.24	2.5	10.3	0.294	0.433	0.139	0.47	0.76	1.04	0.28	0.37

Table A-20 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
ST2981B	0.24	2.5	10.4	0.485	0.466	-0.018	-0.04	1.35	1.30	-0.05	-0.03
OC1481B	0.29	2.9	9.9	0.458	0.535	0.077	0.17	1.48	1.69	0.22	0.15
ST0381B	0.23	2.0	8.6	0.611	0.477	-0.134	-0.22	1.70	1.53	-0.17	-0.10
ST1081B	0.24	1.0	4.1	0.626	0.447	-0.180	-0.29	1.36	1.09	-0.27	-0.20
JL0882R	0.29	2.1	7.3	0.598	0.627	0.029	0.05	1.25	1.43	0.18	0.15
JL0882B	0.28	2.1	7.4	0.541	0.608	0.067	0.12	1.12	1.38	0.26	0.24
Group Average	0.28	2.4	9.0	0.503	0.462	-0.041	0.09	1.32	1.28	-0.04	0.03
S. Dev.	0.08	0.6	3.0	0.175	0.137	0.139	0.92	0.40	0.30	0.27	0.32
Avg. Abs. Value						0.109	0.38			0.22	0.20
S. Dev.						0.094	0.83			0.15	0.25

Table A-20 (Continued)

Experiment	Half-Life PROPENE Expt (min)	Half-Life PROPENE Calc (min)	Half-Life PROPENE Calc -Expt (min)	Half-Life PROPENE Calc -Expt /Expt	Half-Life M-XYL Expt (min)	Half-Life M-XYL Calc (min)	Half-Life M-XYL Calc -Expt (min)	Half-Life M-XYL Calc -Expt /Expt
1. SAPRC EC - 7 HYDROCARBON SURROGATE								
EC231	99	99	0	0.00	136	151	15	0.11
EC232	163	180	17	0.10	204	228	24	0.12
EC233	97	90	-7	-0.07	198	175	-23	-0.12
EC237	85	106	21	0.25	136	159	23	0.17
EC238	141	145	4	0.03	186	191	5	0.03
EC241	142	142	0	0.00	180	177	-3	-0.02
EC242	57	61	4	0.07	118	155	37	0.31
EC243	61	70	9	0.15	108	124	16	0.15
EC245	84	87	3	0.04	108	131	23	0.21
EC246	167	175	8	0.05	218	234	16	0.07
EC247	82	96	14	0.17	112	132	20	0.18
Group Average	107	113	6	0.07	154	168	13	0.11
S. Dev.	39	40	8	0.09	42	37	16	0.12
Avg. Abs. Value			7	0.08			18	0.13
S. Dev.			6	0.08			9	0.08
2. SAPRC ITC - SAI SURROGATE								
ITC626	165	152	-13	-0.08	220	212	-8	-0.04
ITC630	230	233	3	0.01	312	303	-9	-0.03
ITC631	267	312	45	0.17	346	381	35	0.10
ITC633	272	276	4	0.01	363	387	24	0.07
ITC635	353	403	50	0.14	490	541	51	0.10
ITC637	151	155	4	0.03	202	215	13	0.06
ITC865	155	109	-46	-0.30	189	148	-41	-0.22
ITC867	133	90	-43	-0.32	181	119	-62	-0.34
ITC868	146	179	33	0.23	186	229	43	0.23
ITC871	224	197	-27	-0.12		240		
ITC872	180	157	-23	-0.13	233	186	-47	-0.20
ITC873	243	225	-18	-0.07	240	262	22	0.09
ITC874	255	217	-38	-0.15	349	254	-95	-0.27
ITC877	210	156	-54	-0.26	258	184	-74	-0.29
ITC880	347	281	-66	-0.19		334		
ITC881	288	235	-53	-0.18		274		
ITC885		282				324		
ITC886	332	311	-21	-0.06		362		
ITC888	193	150	-43	-0.22	262	192	-70	-0.27
ITC891	158	126	-32	-0.20	220	168	-52	-0.24
Group Average	226	212	-17	-0.09	270	265	-18	-0.08
S. Dev.	70	80	33	0.16	86	100	47	0.19
Avg. Abs. Value			32	0.15			43	0.17
S. Dev.			18	0.09			25	0.10

Table A-20 (Continued)

Experiment	Half-Life PROPENE Expt (min)	Half-Life PROPENE Calc (min)	Half-Life PROPENE Calc -Expt (min)	Half-Life PROPENE Calc -Expt /Expt	Half-Life M-XYL Expt (min)	Half-Life M-XYL Calc (min)	Half-Life M-XYL Calc -Expt (min)	Half-Life M-XYL Calc -Expt /Expt
3. SAPRC OTC - SAI SURROGATE								
OTC189A	120	139	19	0.16	151	173	22	0.15
OTC189B	128	138	10	0.08	150	170	20	0.13
OTC190A	95	135	40	0.42	132	170	38	0.29
OTC190B	108	148	40	0.37	130	186	56	0.43
OTC192A	101	137	36	0.36	139	175	36	0.26
OTC192B	115	158	43	0.37	151	204	53	0.35
OTC194A	75	77	2	0.03	137	109	-28	-0.20
OTC194B	134	136	2	0.01	164	174	10	0.06
OTC195A	135	200	65	0.48	171	267	96	0.56
OTC195B	93	120	27	0.29	111	155	44	0.40
OTC196B	107	141	34	0.32	146	170	24	0.16
OTC197A	104	142	38	0.37	133	189	56	0.42
OTC197B	109	227	118	1.08	205	287	82	0.40
OTC198A	99	148	49	0.49	140	207	67	0.48
OTC198B	95	131	36	0.38	120	186	66	0.55
OTC199A	108	144	36	0.33	128	182	54	0.42
OTC199B	120	148	28	0.23	145	187	42	0.29
OTC202A	66	109	43	0.65	88	177	89	1.01
OTC202B	182	146	-36	-0.20	154	182	28	0.18
OTC203A	169	203	34	0.20	235	283	48	0.20
OTC203B	153	134	-19	-0.12	181	180	-1	-0.01
OTC204A	86	128	42	0.49	159	204	45	0.28
OTC204B	116	115	-1	-0.01	154	149	-5	-0.03
OTC205A	170	239	69	0.41				
OTC205B	81	93	12	0.15	124	123	-1	-0.01
OTC215A	128	145	17	0.13	152	186	34	0.22
OTC215B	89	94	5	0.06	133	123	-10	-0.08
OTC217A	154	177	23	0.15	188	214	26	0.14
OTC217B	112	137	25	0.22	149	172	23	0.15
OTC221A	188	217	29	0.15	226	250	24	0.11
OTC221B	264	238	-26	-0.10	288	280	-8	-0.03
OTC222A	138	127	-11	-0.08		147		
OTC222B	236	76	-160	-0.68		89		
OTC223A	129	133	4	0.03	168	167	-1	-0.01
OTC223B	151	161	10	0.07	255	195	-60	-0.24
OTC224A	137	145	8	0.06	120	176	56	0.47
OTC224B	99	113	14	0.14	141	144	3	0.02
OTC226A	152	183	31	0.20				
OTC228A	198	178	-20	-0.10	280	209	-71	-0.25
OTC228B	151	131	-20	-0.13	283	153	-130	-0.46

Table A-20 (Continued)

Experiment	Half-Life PROPENE Expt (min)	Half-Life PROPENE Calc (min)	Half-Life PROPENE Calc -Expt (min)	Half-Life PROPENE Calc -Expt /Expt	Half-Life M-XYL Expt (min)	Half-Life M-XYL Calc (min)	Half-Life M-XYL Calc -Expt (min)	Half-Life M-XYL Calc -Expt /Expt
OTC229A	142	183	41	0.29		218		
OTC229B		187			276	223	-53	-0.19
OTC230A	162	143	-19	-0.12	187	171	-16	-0.09
OTC230B		166			243	195	-48	-0.20
OTC237A	135	159	24	0.18	156	199	43	0.28
OTC237B	148	171	23	0.16	168	209	41	0.24
OTC238A	160	193	33	0.21	206	240	34	0.17
OTC238B	117	129	12	0.10	172	164	-8	-0.05
OTC239A	136	161	25	0.18	138	194	56	0.41
OTC239B	189	241	52	0.28	273	291	18	0.07
OTC240A	232	275	43	0.19		333		
OTC240B	197	240	43	0.22	242	291	49	0.20
OTC241A	107	146	39	0.36	187	188	1	0.01
OTC241B	113	115	2	0.02	154	147	-7	-0.05
OTC242A	183	228	45	0.25	218	272	54	0.25
OTC242B		171			177	207	30	0.17
OTC243A	230	275	45	0.20				
OTC243B	220	233	13	0.06		358		
OTC248A	313	330	17	0.05				
OTC248B	222	225	3	0.01				
OTC249A	162	203	41	0.25	186	312	126	0.68
OTC249B	155	155	0	0.00	209	211	2	0.01
Group Average	144	164	19	0.18	175	200	22	0.17
S. Dev.	49	50	35	0.24	49	54	44	0.26
Avg. Abs. Value			30	0.23			39	0.24
S. Dev.			26	0.19			29	0.20

Table A-20 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
1. SAPRC EC - 7 HYDROCARBON SURROGATE								
EC231	0.095	0.116	0.021	0.22	0.453	0.410	-0.043	-0.10
EC232	0.040	0.052	0.012	0.30	0.157	0.126	-0.031	-0.20
EC233	0.037	0.043	0.007	0.18	0.145	0.104	-0.041	-0.28
EC237	0.100	0.110	0.010	0.10	0.387	0.362	-0.024	-0.06
EC238	0.113	0.131	0.017	0.15	0.404	0.432	0.028	0.07
EC241	0.047	0.046	-0.001	-0.02	0.137	0.218	0.081	0.59
EC242	0.140	0.145	0.005	0.03	0.673	0.658	-0.015	-0.02
EC243	0.100	0.131	0.031	0.31	0.571	0.680	0.109	0.19
EC245	0.194	0.215	0.021	0.11	0.778	0.784	0.006	0.01
EC246	0.070	0.070	0.000	0.00	0.121	0.124	0.003	0.03
EC247	0.106	0.113	0.007	0.07	0.377	0.406	0.030	0.08
Group Average	0.095	0.107	0.012	0.13	0.382	0.391	0.009	0.03
S. Dev.	0.047	0.052	0.010	0.11	0.228	0.238	0.050	0.23
Avg. Abs. Value			0.012	0.14			0.037	0.15
S. Dev.			0.010	0.11			0.032	0.17
2. SAPRC ITC - SAI SURROGATE								
ITC626	0.116	0.071	-0.045	-0.38	0.045	0.130	0.085	1.89
ITC630	0.027	0.024	-0.003	-0.12	0.025	0.058	0.033	1.32
ITC631	0.002	0.002	0.000	-0.24	0.069	0.029	-0.040	-0.58
ITC633	0.034	0.041	0.007	0.21	0.031	0.108	0.076	2.44
ITC635	0.001	0.002	0.001	0.75	0.092	0.093	0.001	0.02
ITC637	0.117	0.072	-0.045	-0.38	0.127	0.132	0.005	0.04
ITC865		0.065			0.208	0.166	-0.042	-0.20
ITC867		0.049			0.224	0.218	-0.006	-0.03
ITC868		0.042			0.107	0.087	-0.020	-0.19
ITC871		0.018			0.052	0.064	0.012	0.23
ITC872		0.010			0.111	0.105	-0.006	-0.05
ITC873		0.004			0.028	0.041	0.014	0.49
ITC874		0.007			0.079	0.052	-0.028	-0.35
ITC877		0.011			0.113	0.102	-0.011	-0.10
ITC880		0.002			0.014	0.056	0.042	3.00
ITC881		0.001			0.089	0.084	-0.006	-0.06
ITC885		0.001			0.014	0.035	0.021	1.53
ITC886		0.001			0.067	0.039	-0.028	-0.42
ITC888		0.045			0.154	0.125	-0.030	-0.19
ITC891		0.065			0.069	0.147	0.077	1.11
Group Average	0.049	0.027	-0.014	-0.03	0.086	0.093	0.008	0.49
S. Dev.	0.054	0.027	0.024	0.44	0.059	0.049	0.038	1.03
Avg. Abs. Value			0.017	0.35			0.029	0.71
S. Dev.			0.022	0.22			0.025	0.88

Table A-20 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
3. SAPRC OTC - SAI SURROGATE								
OTC189A	0.021	0.075	0.054	2.56	0.199	0.159	-0.039	-0.20
OTC189B	0.025	0.072	0.047	1.88	0.157	0.165	0.008	0.05
OTC190A	0.026	0.060	0.034	1.30	0.276	0.151	-0.125	-0.45
OTC190B	0.018	0.059	0.041	2.27	0.228	0.147	-0.081	-0.36
OTC192A	0.056	0.072	0.016	0.29	0.255	0.165	-0.090	-0.35
OTC192B	0.058	0.072	0.014	0.24	0.284	0.157	-0.128	-0.45
OTC194A	0.100	0.105	0.005	0.05	0.251	0.321	0.070	0.28
OTC194B	0.055	0.061	0.006	0.11	0.190	0.139	-0.051	-0.27
OTC195A	0.007	0.004	-0.003	-0.36	0.069	0.072	0.003	0.05
OTC195B	0.055	0.066	0.011	0.20	0.171	0.163	-0.008	-0.05
OTC196B	0.011	0.009	-0.002	-0.18	0.207	0.167	-0.040	-0.19
OTC197A	0.062	0.057	-0.005	-0.09	0.186	0.132	-0.054	-0.29
OTC197B	0.010	0.005	-0.005	-0.52	0.213	0.122	-0.091	-0.43
OTC198A	0.087	0.084	-0.003	-0.03	0.426	0.275	-0.151	-0.35
OTC198B	0.059	0.039	-0.020	-0.33	0.253	0.144	-0.109	-0.43
OTC199A	0.057	0.052	-0.005	-0.09	0.205	0.146	-0.059	-0.29
OTC199B	0.055	0.040	-0.015	-0.27	0.215	0.145	-0.070	-0.33
OTC202A	0.086	0.072	-0.014	-0.17	0.219	0.261	0.041	0.19
OTC202B	0.046	0.047	0.001	0.01	0.123	0.138	0.014	0.12
OTC203A	0.016	0.025	0.009	0.55	0.178	0.130	-0.048	-0.27
OTC203B	0.026	0.055	0.029	1.11	0.221	0.137	-0.084	-0.38
OTC204A	0.049	0.037	-0.012	-0.24	0.251	0.142	-0.109	-0.43
OTC204B	0.061	0.048	-0.013	-0.21	0.203	0.137	-0.066	-0.32
OTC205A	0.010	0.004	-0.006	-0.57	0.184	0.124	-0.060	-0.33
OTC205B	0.046	0.044	-0.002	-0.04	0.224	0.151	-0.073	-0.33
OTC215A	0.125	0.096	-0.029	-0.23	0.554	0.205	-0.350	-0.63
OTC215B	0.123	0.082	-0.041	-0.33	0.831	0.296	-0.535	-0.64
OTC217A	0.068	0.056	-0.012	-0.18	0.237	0.176	-0.062	-0.26
OTC217B	0.121	0.100	-0.021	-0.18	0.291	0.203	-0.088	-0.30
OTC221A	0.036	0.032	-0.004	-0.11	0.154	0.107	-0.047	-0.30
OTC221B	0.050	0.049	-0.001	-0.03	0.160	0.121	-0.040	-0.25
OTC222A	0.030	0.047	0.017	0.56	0.261	0.158	-0.104	-0.40
OTC222B	0.031	0.044	0.013	0.41	0.253	0.220	-0.033	-0.13
OTC223A	0.054	0.057	0.003	0.06	0.421	0.205	-0.216	-0.51
OTC223B	0.051	0.047	-0.004	-0.07	0.198	0.155	-0.043	-0.22
OTC224A	0.046	0.051	0.005	0.11	0.267	0.171	-0.096	-0.36
OTC224B	0.062	0.068	0.006	0.10	0.234	0.217	-0.016	-0.07
OTC226A	0.040	0.017	-0.023	-0.57	0.012	0.125	0.113	9.48
OTC228A	0.034	0.036	0.002	0.06	0.063	0.107	0.044	0.70
OTC228B	0.025	0.030	0.005	0.22	0.117	0.131	0.014	0.12
OTC229A	0.027	0.040	0.013	0.46	0.113	0.136	0.023	0.21
OTC229B	0.023	0.038	0.015	0.65	0.059	0.115	0.055	0.93
OTC230A	0.038	0.054	0.016	0.42	0.133	0.161	0.028	0.21

Table A-20 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
OTC230B	0.024	0.038	0.014	0.57	0.073	0.123	0.050	0.69
OTC237A	0.064	0.080	0.016	0.25	0.216	0.213	-0.002	-0.01
OTC237B	0.046	0.066	0.020	0.43	0.226	0.201	-0.025	-0.11
OTC238A	0.047	0.050	0.003	0.07	0.139	0.141	0.002	0.02
OTC238B	0.053	0.065	0.012	0.22	0.230	0.203	-0.026	-0.11
OTC239A	0.017	0.025	0.008	0.45	0.166	0.152	-0.014	-0.08
OTC239B	0.017	0.008	-0.009	-0.55	0.129	0.109	-0.020	-0.16
OTC240A	0.001	0.001	0.000	-0.32	0.075	0.063	-0.012	-0.16
OTC240B	0.008	0.003	-0.005	-0.61	0.077	0.085	0.008	0.11
OTC241A	0.064	0.069	0.005	0.08	0.218	0.176	-0.042	-0.19
OTC241B	0.047	0.054	0.007	0.14	0.226	0.188	-0.038	-0.17
OTC242A	0.020	0.012	-0.008	-0.38	0.123	0.089	-0.034	-0.28
OTC242B	0.038	0.056	0.018	0.46	0.129	0.156	0.027	0.21
OTC243A	0.021	0.032	0.011	0.53	0.152	0.170	0.017	0.11
OTC243B	0.022	0.022	0.000	0.02	0.178	0.163	-0.015	-0.08
OTC248A	0.012	0.007	-0.005	-0.39	0.133	0.098	-0.035	-0.26
OTC248B	0.013	0.009	-0.004	-0.34	0.166	0.127	-0.040	-0.24
OTC249A	0.065	0.054	-0.011	-0.18	0.240	0.195	-0.044	-0.18
OTC249B	0.045	0.044	-0.001	-0.03	0.265	0.227	-0.038	-0.14
Group Average	0.044	0.047	0.003	0.15	0.208	0.159	-0.049	0.01
S. Dev.	0.028	0.025	0.017	0.61	0.120	0.050	0.093	1.26
Avg. Abs. Value			0.012	0.39			0.066	0.42
S. Dev.			0.012	0.49			0.082	1.18

4. UNC CHAMBER - UNCMXS

Experiment	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
ST2081R		0.063		
DE0782R	0.010	0.066	0.056	5.35
AU2681R	0.020	0.018	-0.002	-0.11
AU2681B	0.014	0.025	0.010	0.72
AU2781B		0.023		
ST0381R		0.018		
ST1081R		0.063		
ST2081B		0.024		
JL2081B	0.004	0.002	-0.002	-0.48
ST1682R	0.015	0.023	0.008	0.56
JL2081R	0.037	0.017	-0.019	-0.53
JL2281B	0.097	0.071	-0.026	-0.27
OC1481R	0.137	0.075	-0.061	-0.45
ST1682B	0.047	0.084	0.036	0.76
ST2981R		0.078		
ST2981B		0.112		

Table A-20 (Continued)

Experiment	Maximum Concentration PAN				Maximum Concentration HCHO			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt
OC1481B	0.117	0.103	-0.014	-0.12				
ST0381B		0.100						
ST1081B		0.047						
JL0882R	0.085	0.073	-0.011	-0.14				
JL0882B	0.072	0.067	-0.005	-0.07				
Group Average	0.055	0.055	-0.003	0.44				
S. Dev.	0.046	0.033	0.030	1.61				
Avg. Abs. Value			0.021	0.79				
S. Dev.			0.020	1.45				

Table A-21

UNC AUTO EXHAUST RUNS

Experiment	Initial Concentrations NOx (ppm)	Initial Concentrations HC (ppmC)	Initial Concentrations HC/NOx	Maximum Concentration OZONE Expt (ppm)	Maximum Concentration OZONE Calc (ppm)	Maximum Concentration OZONE Calc -Expt (ppm)	Maximum Concentration OZONE Calc -Expt /Expt	Average Initial d([O3] - [NO])/dt Expt --	Average Initial d([O3] - [NO])/dt Calc (ppb/min)	Average Initial d([O3] - [NO])/dt Calc -Expt --	Average Initial d([O3] - [NO])/dt Calc -Expt /Expt
1. UNC CHAMBER - VOLARE											
JN2582R	0.65	0.6	0.9	0.003	0.011	0.008		0.64	0.64	0.00	-0.01
JN2582B	0.65	0.6	0.9	0.003	0.011	0.008		0.68	0.65	-0.03	-0.05
JN2982R	0.24	2.5	10.3	0.704	0.689	-0.015	-0.02	2.32	2.51	0.19	0.08
JN2982B	0.25	2.5	9.8	0.766	0.695	-0.071	-0.09	2.67	2.55	-0.12	-0.05
JN3082R	0.32	2.8	8.7	0.811	0.761	-0.049	-0.06	2.55	3.38	0.83	0.33
JN3082B	0.32	0.6	1.7	0.840	0.777	-0.063	-0.08	2.68	3.29	0.61	0.23
JL0283B	0.19	1.7	9.1	0.697	0.707	0.010	0.01	1.65	1.87	0.22	0.13
JL0883B	0.37	1.7	4.6	0.879	0.705	-0.173	-0.20	1.76	1.44	-0.32	-0.18
ST2982B	0.39	1.7	4.3	0.205	0.097	-0.108	-0.53	1.12	0.90	-0.23	-0.20
OC0682R	0.46	2.0	4.3	0.355	0.240	-0.116	-0.33	1.37	1.27	-0.10	-0.07
AU1183R	0.22	2.2	9.9	0.850	0.743	-0.107	-0.13	2.55	2.34	-0.21	-0.08
AU1183B	0.23	0.7	3.1	0.601	0.516	-0.084	-0.14	1.26	1.13	-0.13	-0.10
Group Average	0.36	1.6	5.7	0.559	0.496	-0.063	-0.16	1.77	1.83	0.06	0.00
S. Dev.	0.16	0.8	3.7	0.330	0.312	0.058	0.16	0.77	0.97	0.35	0.16
Avg. Abs. Value						0.068	0.16			0.25	0.13
S. Dev.						0.053	0.16			0.24	0.09
2. UNC CHAMBER - CHARGR											
JL0182R	0.37	3.5	9.6	0.740	0.865	0.126	0.17	2.31	3.07	0.75	0.33
JL0182B	0.35	3.6	10.2	0.759	0.824	0.065	0.09	2.41	3.28	0.88	0.36
AU0382R	0.44	2.5	5.7	0.344	0.334	-0.010	-0.03	1.26	1.33	0.07	0.06
AU0382B	0.16	1.2	7.3	0.576	0.445	-0.131	-0.23	1.06	0.87	-0.19	-0.18
ST1782R	0.26	2.2	8.6	0.562	0.562	0.000	0.00	1.63	1.29	-0.34	-0.21
ST1782B	0.25	2.4	9.5	0.637	0.585	-0.052	-0.08	1.72	1.38	-0.33	-0.19
ST2982R	0.39	1.7	4.4	0.073	0.082	0.009	0.12	0.86	0.84	-0.02	-0.02
OC0682B	0.46	2.0	4.3	0.450	0.276	-0.173	-0.39	1.49	1.34	-0.15	-0.10
JL0283R	0.18	1.6	9.0	0.595	0.596	0.001	0.00	1.37	1.44	0.06	0.05
JL0883R	0.37	1.7	4.6	0.756	0.543	-0.213	-0.28	1.52	1.30	-0.23	-0.15
JL1583R	0.35	2.2	6.2	0.866	0.654	-0.211	-0.24	2.10	1.74	-0.35	-0.17
JL1583B	0.35	2.3	6.6	0.922	0.759	-0.163	-0.18	2.20	2.07	-0.13	-0.06
OC0483R	0.25	2.6	10.3	0.603	0.651	0.049	0.08	1.76	1.91	0.15	0.08
Group Average	0.32	2.3	7.4	0.606	0.552	-0.054	-0.07	1.67	1.68	0.01	-0.02
S. Dev.	0.09	0.7	2.2	0.226	0.222	0.112	0.17	0.48	0.75	0.39	0.19
Avg. Abs. Value						0.092	0.15			0.28	0.15
S. Dev.						0.080	0.12			0.26	0.11

Table A-21 (Continued)

Experiment	Initial Concentrations			Maximum Concentration OZONE				Average Initial d([O3] - [NO])/dt			
	NOx (ppm)	HC (ppmC)	HC/NOx	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt --	Calc (ppb/min)	Calc -Expt --	Calc -Expt /Expt
3. UNC CHAMBER - SYNEXH											
OC0483B	0.25	0.4	1.7	0.642	0.695	0.053	0.08	1.86	2.11	0.26	0.14
OC0783R	0.33	2.7	8.1	0.178	0.430	0.252	1.41	0.94	1.39	0.46	0.49
OC0783B	0.34	2.7	7.9	0.451	0.656	0.206	0.46	1.41	2.18	0.76	0.54
Group Average	0.31	1.9	5.9	0.424	0.594	0.170	0.65	1.40	1.89	0.49	0.39
S. Dev.	0.05	1.3	3.6	0.233	0.143	0.104	0.68	0.46	0.44	0.26	0.22
Avg. Abs. Value						0.170	0.65			0.49	0.39
S. Dev.						0.104	0.68			0.26	0.22

Table A-21 (Continued)

Experiment	Maximum Concentration PAN				Half-Life ETHENE			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
1. UNC CHAMBER - VOLARE								
JN2582R	0.004	0.001	-0.003	-0.76	692			
JN2582B	0.004	0.001	-0.003	-0.74				
JN2982R	0.065	0.056	-0.008	-0.13		334		
JN2982B	0.070	0.060	-0.010	-0.14		331		
JN3082R	0.068	0.098	0.030	0.44	325	309	-16	-0.05
JN3082B	0.068	0.095	0.026	0.38	339	311	-28	-0.08
JL0283B	0.043	0.036	-0.007	-0.17	345	328	-17	-0.05
JL0883B	0.081	0.028	-0.053	-0.66	433	448	15	0.03
ST2982B	0.014	0.005	-0.009	-0.64				
OC0682R	0.024	0.013	-0.011	-0.45		557		
AU1183R	0.032	0.042	0.011	0.35	326	326	0	0.00
AU1183B	0.010	0.008	-0.002	-0.17	346	388	42	0.12
Group Average	0.040	0.037	-0.003	-0.22	400	370	0	0.00
S. Dev.	0.029	0.034	0.021	0.44	133	82	25	0.07
Avg. Abs. Value			0.014	0.42			19	0.06
S. Dev.			0.015	0.24			14	0.04
2. UNC CHAMBER - CHARGR								
JL0182R	0.076	0.081	0.005	0.07	359	321	-38	-0.11
JL0182B	0.079	0.089	0.010	0.12	361	315	-46	-0.13
AU0382R	0.007	0.014	0.006	0.81	513	533	20	0.04
AU0382B	0.012	0.015	0.003	0.24	389	405	16	0.04
ST1782R	0.042	0.042	0.000	0.00	336	396	60	0.18
ST1782B	0.045	0.043	-0.002	-0.04	354	395	41	0.12
ST2982R	0.006	0.005	-0.001	-0.19	479			
OC0682B	0.026	0.015	-0.012	-0.44	479	534	55	0.11
JL0283R	0.041	0.033	-0.009	-0.21	337	323	-14	-0.04
JL0883R	0.092	0.031	-0.061	-0.66	515	441	-74	-0.14
JL1583R	0.068	0.041	-0.027	-0.40	363	355	-8	-0.02
JL1583B	0.063	0.051	-0.011	-0.18	376	339	-37	-0.10
OC0483R	0.061	0.054	-0.007	-0.12	373	312	-61	-0.16
Group Average	0.048	0.039	-0.008	-0.08	402	389	-7	-0.02
S. Dev.	0.029	0.025	0.019	0.36	67	79	45	0.11
Avg. Abs. Value			0.012	0.27			39	0.10
S. Dev.			0.016	0.24			21	0.05

Table A-21 (Continued)

Experiment	Maximum Concentration PAN				Half-Life ETHENE			
	Expt (ppm)	Calc (ppm)	Calc -Expt (ppm)	Calc -Expt /Expt	Expt (min)	Calc (min)	Calc -Expt (min)	Calc -Expt /Expt
3. UNC CHAMBER - SYNEXH								
OC0483B	0.060	0.056	-0.005	-0.08	335	304	-31	-0.09
OC0783R	0.056	0.062	0.006	0.12		429		
OC0783B	0.101	0.092	-0.009	-0.09	408	314	-94	-0.23
Group Average	0.072	0.070	-0.002	-0.02	371	349	-62	-0.16
S. Dev.	0.025	0.019	0.008	0.12	51	69	44	0.10
Avg. Abs. Value			0.007	0.09			62	0.16
S. Dev.			0.002	0.02			44	0.10